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DEPOSITION OF MANGANESE.

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I. INTRODUCTION.

The experiments on which this treatise is based were made by the writer for the purpose of developing a method of extracting manganese from the water supply of the City of Brainerd, Minnesota, and are primarily of value to water-works engineers, but geologists interested in sedimentary rocks and ore-deposits, or water-supply problems in their States, should find in them much of interest and importance. As a member of the Water and Light Board, which has charge of the public utilities, the writer urged in 1915 the development of a new water system. The use of water taken from the Mississippi River was discontinued and, instead, gravel-beds in the glacial drift were tapped. By 1921 a whole new system, including wells, reservoirs, distribution

mains, and the placing of meters on every service-line, was completed. The water is neither treated nor filtered.

While drilling was in progress, water-samples were analyzed by the State Board of Health for hardness, alkalinity, iron, chlorine and incrustants. Authorities, including text books on public water-supplies that were consulted, provided the information that water should not contain more than 0.5 p.p.m. of iron, otherwise, it was said, sediment would form in pipes, lavatory fixtures would show iron stains, and white clothes would launder yellowish. Inasmuch as the samples of Brainerd water analyzed about 0.30 p.p.m., the water was deemed good in that respect. No analyses were made for manganese; and, as will be shown later, at that time (about 1916), manganese was hardly known in relation to water-supplies.

Before the new plant was in operation a year, yellow staining was noticeable. New analyses of the water pumped then showed that the iron-content was from 1.0 to 1.2 p.p.m. By the second year, meters were stopping and certain service-lines showed diminishing flows. The solid material deposited in pipes and meters was readily identified by the writer as an oxide of manganese forming about three-fourths of the thickness with some oxide of iron. To combat the manganese necessitated making experiments and developing a method of demanganization. Manganese can be precipitated, let it be understood, by using chemicals; but in a municipal supply, water should not be treated with chemicals and made worse in other respects just for the sake of removing the manganese. Also, it is one thing to remove manganese in a beaker using filter paper, and quite another thing to treat water in a plant at the rate of 1,000,000 gallons per day, avoid causing interruptions, use mechanical filters, and do it cheaply.

The first experimental work was done indoors, in the winter of 1928. Somewhat bulky equipment rather than laboratory glassware was used, to compare with materials in the system, and then the essential facts as to manganese precipitation were obtained. In the summer of 1929 an experimental plant was built

outdoors, and was operated mainly to corroborate the results previously obtained indoors and to develop engineering data. In 1930 the same unit was operated continuously from April to December to determine permissible variations in the set-up, the time factors and vagaries of the process, the manipulation of equipment, and to enable a building to be designed for erection in 1931. Samples analyzed number many hundred, and all analyses were made by competent commercial analysts, none of whom were concerned in the tests or the samples taken.

Concurrently with the experimental work made last, in 1929 and 1930, a comprehensive review was made of the voluminous literature regarding manganese in water and its removal. Much of it is published in the German language. As a whole, the publications offer so many contradictory statements and opposite conclusions, with successive repetitions, and so little is given regarding practical applications, that no effort will be made to quote references in this treatise; however, a list of publications is appended containing references that the writer deems most useful to those interested in this subject.

Everything done in the Brainerd tests was executed without reference to what others had attempted. Where others, after extensive tests, concluded that all manganese could not be removed and described restrictions, it was at the outset incontrovertible that manganese was being deposited in the Brainerd mains and that extraction was complete. It was the purpose in these experiments to accomplish demanganization in the same way that nature was doing it; and when this secret of nature could be obtained, to simulate above ground what nature was doing in the pipes below ground. This was the basis on which these tests were planned and carried out. In the Brainerd tests both manganese and iron were reduced to "traces" and it was accomplished without in any way detracting from the sparkle and snap of fresh water.

The conditions involved in the deposition of manganese ascertained by this investigation are duplicated again and again in nature and can be seen in operation; this experimental work is,

therefore, believed to provide the explanation of the origin of certain deposits of manganese ore, the composition of certain sedimentary formations, and the more local phenomenon of concretions. What has been overlooked in a water system may also have been overlooked or minimized in geology. The simplicity of it all baffles the individual.

HISTORY.

Much consideration has been given in late years to the activity of bacteria as precipitating agents of iron and manganese. This special group is spoken of as thread-bacteria; they are also called the iron-bacteria, because iron oxide is always seen in or on them and they are invariably found in places where iron oxide is being deposited.

The first of such thread bacteria, *Gallionella ferruginea* (Ehrenberg),[1] was discovered in 1836; then *Leptothrix ochracea* (Kützing), in 1843; then *Crenothrix polyspora* (Cohn), in 1870, and *Cladothrix dichotoma* (Cohn), in 1875, the latter being, however, soil bacteria. In 1904 B. Schorler described *Clonothrix fusca* (Schorler) and the last important species of these bacteria was identified by David Ellis in 1911, namely, *Spirophyllum ferrugineum* (Ellis). Between 1870 and 1910 studies and discussions centered on physiology and morphology, and especially on the question of whether these organisms attacked iron salts to obtain the iron for nourishment or whether the iron oxide, always in evidence, was a residue of their activities. In Europe these organisms came to play an important part in investigations for practical deferrization and demanganization of waters.

Although manganese has been known as an element since 1774 it was not referred to as a constituent of ground waters until 1896. This discovery seemingly did not receive notice until 1906, the year in which the City of Breslau, Germany, as a result of a flood condition in the Oder River valley, experienced a serious catastrophe with its water supply. In 1892 the biologist, Hans

[1] References to names quoted in this paper will be found in the Bibliography at the end of the article. In cases of two or more articles under one name, the date will distinguish them.

Molisch, first noted that manganese was present in a bacteria culture, but no analysis was made of the water. The Breslau catastrophe was a serious matter and quick corrective measures were needed. Biologists had not yet progressed far enough to slip into the breach forcefully. The chemist was commandeered and prescribed several inorganic methods. He showed that simple æration would not suffice; that the addition of lime or potassium permanganate would remove manganese, but both salts introduced new troubles. Before the chemists had concluded their investigations the flood subsided and the ground-water had restored itself to normality. There were now two conflicting schools of thought, the one advocating bio-chemical action and the other inorganic chemical action. Manganese was thereafter commonly noted in ground water. In Europe most waters have to be filtered for sanitary reasons, and when, in 1911, the City of Dresden built several treating plants, it actually used cultures of bacteria on the filter beds to remove iron and manganese. However, in that one Dresden plant in which the manganese-content of water was the highest, the organisms were not equal to the occasion and aid had to be supplied by supplementing an inorganic agent, which is of significance.

During the next few years, say from 1908 to 1912, certain chemists devoted themselves to quick and reliable methods for the determination of manganese in waters. The necessity of this is quickly appreciated when it is realized that amounts of less than 1.0 p.p.m. in water supplies are exceedingly troublesome, and in operating plants analytical checks must be made quickly, without resorting to the old method and necessity of first boiling down large quantities of water to obtain a concentrated solution or residue. This analytical work by chemists represents another stage in the study of demanganization.

About 1912, engineers began tests. In nearly all these instances it is evident that the engineer-investigator proceeded on the theory that manganese can be removed by the same method used for deferrization. Removing iron is simple, requiring primarily intimate contact with the atmosphere, accomplished by

spraying or cataracting the water in the air. Some experimenters introduced contacting the water with crushed lavas, limestone, or coke, this being another means of ærating water. The ferric hydroxides thereby formed are then coagulated and settled; in some places the water is filtered. As to manganese the results were uniformly unsatisfactory in that not enough manganese, if any, was removed.

To engineers, the bio-chemical method was too slow, requiring several days for results, and the action was not sufficiently understood to be possible of regulation. As to the chemist's proposals, people commonly are averse to treating water with ingredients that create too much alkalinity or too much acidity, or affect the flavor.

There were, therefore, eventually three schools of thought, each championing its own ideas and more or less decrying the ideas of the other. Each could prove some results but none could advance efficacy under all conditions. The conclusions the various experimenters arrived at from their respective investigations, presented many contradictions.

Strangely, indeed, in the comprehensive and various work, iron seems to have been preponderantly made the objective and manganese, it was assumed, would respond to the same treatment. Manganese associated with bacteria has been described fully only in recent years; and in the literature it has been viewed as a secondary matter, except in isolated instances. Is it not true that in America we have become manganese-minded only in the last decade? It is now known that two thread-bacteria grow fat on inorganic manganese salts and attack them in preference to iron salts, that two others at times attack certain manganese salts, and several lower forms are equally effective.

Confusion is easy, since ferric hydrates deposited chemically are slimy, as are the products of bio-chemical activity. Either kind floats along in the mains and finds an exit at faucets in homes, and some of it is caught on projections in pipes en route, or lodges in dead ends. Most iron escapes at outlets eventually. Manganese is deposited by bacteria simultaneously with iron, becomes mixed

with the iron slimes and is discolored by them. Because there is deposition of manganese from another cause as well as biochemical, and it is finely granular, most of the manganese is found as an incrustation in pipes and does not reach the faucet; and as it incorporates some of the ferric slimes in its mass, evidence becomes available and for each theory there is some support and some contradiction. These bacteria are present always and propagate where conditions for the specific kind of organism are favorable. All are delicate organisms and their casts are soon destroyed; and as mixtures of iron and manganese-oxides and hydrates result and are distributed variously, the product or result observed easily disguises the truth. The same is true in deposition in rocks; a water main is merely a means of directing a flow; in other respects reactions are similar.

QUANTITATIVE DATA.

Iron and manganese are both essential to the human blood stream and from that standpoint it may be a mistake to remove these two elements; however, from the standpoint of municipal engineers the main question is: what is an undesirable quantity?

On this question there is in the literature unanimity of opinion. Had manganese been known earlier as a desirable food for bacteria, and had it been recognized earlier as a common constituent of ground- as well as of surface-waters, the statements now in print would unquestionably read otherwise. Long ago bacteriologists pronounced that at least 0.5 p.p.m. of iron was needed for propagation, and virtually every text-book on water-supplies contains the statement that 0.5 p.p.m. of iron is the maximum limit if staining and incrustation are to be avoided. Some publications record instances of pipes clogging when iron was considerably less than 0.5 p.p.m. Unfortunately no statement was made of the amount of manganese present.

It should be impressed on every investigator that both *Crenothrix polyspora* and *Leptothrix ochracea* are capable of building up large quantities of manganese. In all probability deposits in most pipes contain both elements. In short, if the figure 0.5 is an acceptable

figure, it should in all cases be regarded as a sum of iron and manganese. Presumably because most of the laboratory pure cultures used in experimental work have been of *Gallionella,* the figure 0.5 has become well established, because *Gallionella* feeds only on iron salts.

Waters in lakes and rivers have been represented as not containing much iron or manganese. Presumably the information is not as complete as it should be. The higher manganese-contents recorded are usually of waters obtained from wells, especially if the wells are in valley fillings or glacial drift. At Brainerd, the water is obtained from driven tubular wells bottoming in gravel beds of glacial drift. The drift has a maximum depth of 130 to 160 feet and the bed-rock is chloritic schistose slates, and andesitic tuffs, characteristic of the upper horizon of the beds constituting the Cuyuna Iron Ore District. The water pumped from the wells is derived from precipitation, which percolates through about 70 feet of sand before it reaches the gravel horizon.

From analyses obtained over a long period, iron in Brainerd water may be said to amount to no more than 1.2 p.p.m. and manganese 1.0 p.p.m. These quantities are much too large and need be reduced. Manganese even in well waters has not commonly been reported in excess of 2 p.p.m. In 1930 a well was drilled 20 miles from Brainerd, near Ironton, Minn., which showed 146 parts. During the Breslau calamity, the manganese-content was reported variously up to 220 parts. If analyses were made as regularly for manganese as for iron, it might become possible to report more of the higher contents.

As to iron, matters are quite different. Because iron is so easily removed by æration, waters with high contents can be used and reports of such waters are not uncommon. It is not uncommon to read of 5 or 6 parts of iron. When the valley floor of the Breslau water works was flooded the iron-content rose to 440 parts.

The essentials to advance now are that: (1) if only *Gallionella* and *Spirophyllum* and only inorganic salts of iron are present,

0.5 p.p.m. will be enough to create slimes of iron hydrates; (2) if manganese is also present, deposition of manganese and iron is certain if *Crenothrix* and *Leptothrix* are in the waters and, according to E. C. Harder, if iron plus manganese is equal to about 0.2 p.p.m.

Gallionella and *Spirophyllum* will be active if iron and manganese are both present, but they will attack only the iron salts; and it has been demonstrated recently that *Gallionella* may propagate if even less than 0.5 p.p.m. iron is present. *Gallionella* and *Crenothrix* favor pipes as a habitat; but all the thread-bacteria are ever present and they are always in battle formation.

The case is not as simple as stated above, because the kind of iron- and manganese-salt present is a material factor; also the condition of light and darkness, the amount of oxygen present, and the alkalinity or acidity of the water. These matters will not be discussed here, although each condition may arise and each has a material bearing on the organism propagated and the results observed.

Even though mechanical and inorganic methods of removal of manganese were sought for and are to be used, it is impossible to study and discuss deferrization or demanganization without mentioning bacteria, and the same applies to geologic problems. In seeking for the method and in understanding it, the lesson is to be learned from bacteria. Bacteria are either apt to arrive at any time and set the machinery in motion, or they may be present and be on the lookout and ready to go into action as soon as certain conditions develop.

FACTORS CAUSING PRECIPITATION.

Opinions advanced regarding precipitation often seem biased as to a single condition or factor. The following factors have received emphasis.

All ground waters contain occluded oxygen, some more than others. Aerating, by spraying and cataracting the water, enables the water to occlude more oxygen, which then satisfies the unstable bicarbonate of iron and forms an oxide or insoluble

hydrate. Aeration barely affects the bicarbonate of manganese. Thread bacteria need oxygen. Ellis concludes that these bacteria influence the rate of oxidation by liberating substances that affect oxidation as an external process. He does not consider this oxidation a physiological process under the direct control of the protoplasm. Because oxygen is important in mechanical methods, bacteria can be used to help in oxidation. Or, viewed another way, bacteria can make it possible for these salts to become oxidized by the occluded oxygen.

Carbon dioxide in waters has been given much attention by some workers, quite as if it had been made the objective in the problem, and they say the content must be reduced to a very low amount to enable precipitation of iron, because if it is not removed it raises the acidity. If retained, it is also claimed that it will tend to form stable carbonates in solution instead of oxide precipitates. More will be related about this subsequently. J. Tillmans reported that all bacteria keep the carbon dioxide content low. Apparently, we have here another hint from microorganisms.

All writers stress the fact that water must be alkaline. Lime, calcite, and soda have been introduced into waters to produce alkalinity, and water has been trickled through limestone rubble and crushed lava for the same reason. The need of an alkaline condition was proved by chemical experimentation, but the same thing can be learned from observations of bacteria. These bacteria have elastic, mucilaginous sheaths that constitute their outer walls, and perhaps help to give them their cylindrical or thread-like shapes. These sheaths have been shown by Molisch and Schorler to give alkaline reaction. Binz, in 1901, demonstrated the relationship between alkaline reaction in water from which iron is precipitated and the alkalinity caused by certain bacteria and algæ to produce that precipitation. When the bacteria *Crenothrix* and *Leptothrix,* for example, attack the bicarbonate, they desire the carbon for sustenance and, whether correct or not, absorb as a vital force the energy, or heat, created, leaving the metal molecule sticking to the sheath, where, under the natural

alkaline condition, the oxygen in the water or contributed by the organism converts it into a stable oxide of the metal. Alkalinity admittedly is essential to produce the results desired; but there must be some other reason for the unusually high degree of alkalinity advocated by some investigators, because experiments in treating Brainerd water show that here such high alkalinity is not essential. For other reasons, high alkalinity would actually be undesirable.

Hydrogen-ion concentration (pH) has of late been stressed, and invariably a rather high concentration (9 to 10 and even more) has been advocated. Fortunately tests for it can be made quickly on the spot. People who advocate the use of chemical preparations for precipitation of manganese usually strive to develop not less than 9.5 pH concentration. Tillmans concluded that a higher pH could be substituted for a higher oxygen-content in water. It may be, therefore, that some experimenters dabble more with pH rather than with atmospheric æration. The records are not clear. The Brainerd tests disposed of the manganese without resorting to lime or soda ash to produce alkalinity, and the pH in the effluent rarely exceeded 7.5; this is so little over neutral (7.0) that it is worthy of more than just casual notice.

Increasing the acidity has been advocated to destroy the bacteria and prevent precipitation of iron by them. Chlorine will destroy them. Acidity subsequently requires neutralization. Contrariwise, some people advocate making use of bacteria, under control, to precipitate iron. The effectiveness of bacteria in precipitating iron is best shown by the case described by Ellis for a collecting basin in Cheltenham, England. In 1896 the water in this basin turned brown from a prolific growth of *Crenothrix*. It remained so for several weeks. Methods of rectification were studied, but before devised the water clarified itself and then became as good as ever. Obviously, the food supply had first become unusually abundant. *Crenothrix* is a voracious feeder,—it is called the "water-pest,"—and ate itself to death. The sudden occurrence of this super-development of *Crenothrix* is one of those odd phenomena of nature difficult to believe and not freely

drawn upon in explanation of things of the past not actually observed while in process; it demonstrates what a powerful influence these minute organisms exert, also why some people might advocate their destruction, or their use in deferrization plants. Such extreme activities suggest the extent to which bacteria may have played an important part in depositing iron and manganese in geologic periods. In analyses made of *Crenothrix* by Schorler in 1904, manganese was often found to be present in greater amounts than iron. Molisch had shown in 1892 that manganese increased the size of the bacteria. Consequently, manganese need not be viewed as a stranger or an interloper.

A variation of ærating by spraying was introduced by German investigators, about twenty years or more ago. In one instance water was percolated through a thin bed of coke; in the other case thicker beds were used and submerged in water in a quiescent state. In one place crushed natural lava was used, lava at that place probably being easier and cheaper to obtain than coke. Coke and cellular rocks have the same physical properties, and basic lavas would, as well, promote alkalinity. A porous material offers great surface area, and its irregular shapes cause waters to follow devious courses in passing through it. Coke occludes air in the cells and makes for a more intimate or a longer contact. By backwashing, the beds can be refreshed and a new supply of air, or oxygen, introduced.

Geologists may find in all this something comparable to flows of basic igneous rocks into adjacent seas. The bubbling and the explosions caused by heated rocks constitute a form of æration at depths, with alkalinity a natural consequence. Water rushing into a sea is being ærated. Usually the emphasis in geological studies is placed on the contribution of metals made by igneous magmas, whereas a very little iron or manganese in solution obtained by weathering of land surfaces can build up a big mass of sedimentary iron and manganese oxides, provided conditions for precipitation are favorable. Conditions favoring precipitation seem easier to explain than is generally believed; and similarly, the original content of the metal in solution in waters can be sufficient,

though smaller than is usually supposed or advocated in support of a theory made dependent on igneous activity.

"Permutit" is a trade name for a manufactured zeolite. It is most efficaceous for softening water in industrial plants. As a variation, the inventor incorporated about 8 per cent. manganese, in the form of several oxides ($MnO.Mn_2O_7$), and called the new product manganese-permutit. It was used in 1911 in the Dresden filtration plant to aid the bacteria used in removing manganese; also in special high-pressure filters in Breslau and Glogau and nearby places. It had to be energized frequently by treating it with potassium permanganate, or preferably calcium permanganate ($CaMn_2O_8$). H. P. Corson, in 1916, investigated this substance thoroughly and concluded that the zeolite component played no part in precipitating manganese, as the inventor had claimed for it, and that the manganese oxide alone was the potent medium, acting as a catalyzer. J. Tillmans, of Germany, corroborated this at about the same time. Manganese permutit has not come into use in this country, perhaps due to the lack of appreciation of a need for manganese removal, and, maybe, due to its cost. Iron has to be removed first to keep the grains of permutit from becoming coated and thereby weakened.

If removal of a solid substance is required, a filter must be provided. Filters consist of gravel and screened sand, the bed being commonly about three feet thick. Because a coagulant (aluminum sulphate) is invariably used, the top of the bed becomes coated quickly with a floc which retains the solids, and because the latter become obnoxious in one or more respects, the filter beds require almost daily backwashing to cleanse them. That interferes with using bacteria cultures on top of filter beds. Everything about the action of the filter bed is intended to be physical in nature. Glacial deposits are natural filter beds, but some of their constituents can go into solution and give rise to other problems.

ANALYSIS OF BRAINERD WATER.

The analysis given below is typical of several obtained.

	p.pm.
Ammonia nitrogen (N)	0.006
Aluminoid ammonia nitrogen	trace
Nitrites—nitrogen	0.003
Nitrates—nitrogen	0.180
Oxygen consumed, 30 minutes	1.000
H-ion concentration (pH)	7.00
Alkalinity (methyl orange)	198.00
Total Solids (dried 125° C.)	287.00
Insoluble Silica ($SioO_2$)	14.40
Iron (Fe)	1.00
Manganese (Mn)	0.80
Aluminum Oxide (Al_2O_3)	0.57
Chlorine	0.70
Calcium oxide (CaO)	83.00
Magnesium oxide (MgO)	29.25
Sulphur	7.13
Sodium and Potassium Chlorides	29.80
Equivalent of Na and K as Na_2	11.71
Temporary Hardness	209.00
Permanent Hardness	32.00
Total Hardness	241.00

The iron and the manganese in the water total between 1.7 and 2.0, which is up to seven times the permissible quantity. The manganese, taken over a period of years, can be said to average just a little less than the iron present. Pumping one million gallons of water per day means that in one year about 2½ tons of metallic iron and manganese are pumped into the system; but in the form of oxides or hydrates formed, the residual quantity of solids is nearly doubled, say 4 tons, and very little of it finds its way out through points of exit.

DEPOSITS IN PIPES.

Observation of deposits is largely confined everywhere to service pipes and meters, because of the frequency of the plugging and the accessibility. These pipes show a thin layer of shelly yellowish iron oxide along the walls which is overlain by a thick accumulation of manganese oxides mixed with a little iron oxide.

The slimy, sticky character of the precipitated iron facilitates quick attachment to walls of pipes, and the fact that some of the bacteria attach themselves helps also to form a basal layer of iron oxide.

Although some bacteria deposit manganese, manganese is also deposited by another process that produces a finely pulverulent or granular precipitate. Manganese from either origin becomes enmeshed in the soft deposit of iron oxide first formed and then it builds up rapidly by the second process, whereas the iron oxides are always flocculent and seem to flow with the current.

In every system of mains are short stubs, and here the water is preponderantly quiet. Some of the bacteria prefer such a condition, and here iron is deposited in greater quantities than manganese and, when drained, is reddish. The water becomes foul. Manganese found here is due largely to having been forced in during periods of high-pressure pumping.

Because *Gallionella* and *Spirophyllum* are free-swimming bacteria and deposit only iron, iron may for that reason also be found throughout the system, and in certain areas the iron-content in the water in mains becomes higher than at the source.

Casts of *Gallionella* in deposits on walls of pipes have been reported by several investigators; others have undertaken to prove that bacteria are not present in such deposits and have taken no part in the deposition of iron. There is sufficient evidence to show that *Crenothrix* and *Leptothrix* freely deposit manganese.

It is apparent that in commenting on what has been found in the water system, all places and all features of the system should be known and considered. Although the so-called iron-bacteria, including also the lower forms of bacteria in which iron and manganese have of late been detected, are few in number, these few live and propagate under such varied conditions that while one important kind or condition may be absent the remainder may be sufficient to account for all that has happened. It is easily comprehended that casts of such minute and delicate organisms are not to be expected in every deposit, and obviously one would not

expect to find them in any other than the most recent layers of a deposit. The same holds true in geologic formations.

Samples of the deposit of soft material obtained from pipes in three different parts of the city analyzed as follows:

Fe (dried at 212° F.)	13.32%	14.46%	18.48%
Mn (dried at 212° F.)	29.00	29.93	29.07
SiO_2	16.18	7.08	5.48
Al_2O_3	.42	.67	?
CaO	1.79	5.55	2.82
MgO	2.96	.56	.31
Loss on Ignition	18.00	23.52	22.37
Total	81.67%	81.77%	78.53%

If the iron and manganese are figured as oxides, the total percentages approximate 100, therefore these analyses show a composition comparable to low-grade ores of manganese.

The first analysis is high in silica because in the removal of a length of the main, from which the precipitate was taken, considerable sand from the excavation got into the pipe. The sample was seen to be contaminated with sand and a high silica-content was anticipated. This may also account for the magnesia.

There is a remarkable similarity in the general composition of the three samples. Of greatest interest is the fact that although the iron-content in the water at the source is higher than the manganese-content, in these precipitates the manganese-content is virtually twice as high as the iron-content.

The loss on ignition obtained is more than would be needed to satisfy the two metals if they were calculated as hydrates and the two bases as carbonates. The presence of organic matter must account for the excess. At the writer's request, the Minnesota State Board of Health examined several samples of the precipitates, and all the characteristic water-main thread-bacteria were recognized in abundance.

On different occasions a series of samples was taken of waters obtained at the source and at different points along the distribution system, and analyzed for iron and manganese. Taking samples along the route does not constitute a sample of the same initial

specimen as it travels along, but the results were always so similar in their general aspects that one can not avoid taking note of what they disclose. These analyses show what has been repeatedly observed, namely, the loss of manganese along the route and the gain in iron. Manganese was completely precipitated, and precipitation started close to the pumping station. The increase in iron and the loss of manganese with distance is the significant thing.

Another thing observed was that a much larger quantity of sludge was found near the station than farther away. It means that precipitation of manganese takes place rapidly, and it may be concluded that manganese is precipitated largely by some other force than bio-chemical action, regardless of how attractive the latter may be as a cause.

II. EXPERIMENTAL RESULTS.

This treatise has been prepared for geologists, therefore only such of the acquired engineering data are given as provide the counterparts of what may be found in nature as geologic problems. For the sake of brevity the experimental work will not be detailed. The following is offered in the nature of a summary.

As a preliminary statement it should be stated that the progress of the experiments was governed by the fact, learned early in the tests, that the mud-like precipitate obtained from the mains when brought in contact with untreated water and agitated a little to mix it well, resulted in complete precipitation of the two dissolved metals. The remainder of the work was then a matter of collecting the newly created precipitate, obtaining the time of reaction, the necessary quantity relationships, the permissible variations, and the simplest design for a plant.

The experiments showed conclusively that demanganization can be accomplished without resorting to intricate methods or using complicated equipment, and at low cost. The fundamental principles ascertained here have been touched upon separately by various investigators, each of whom had previously investigated some certain phase of the subject, and it is not a local condition because their tests have been conducted in widely separated parts

of the world and with various waters. However, ascertaining certain essentials and assembling all of them in the form of a simple, practical and workable plant designed for demanganization on a large scale had not been accomplished until now. It is an invention and a patent on it has been applied for.

Simple æration has failed, except as to iron. For manganese removal, a strong catalytic agent is needed, and the mineral pyrolusite was found to be effective and possessed with physical advantages. It is a substance easy to obtain and easy to apply. If it shows signs of weakening, it is restored by washing and exposure to air. It promotes alkalinity, which is essential but required to a small degree only.

Aeration, to provide excess oxygen as an assisting agent, is essential. Oxygen can be introduced by several methods. Plunging the water from the inlet-pipe into the pyrolusite, or dropping or cascading water a few feet as it leaves the pyrolusite are two simple and effective methods.

Trickling through a bed of fine coke is efficaceous as an ærator, Coke also promotes alkalinity; but, best of all, its cellular texture enables retention of the $Mn(OH)_4$ or the MnO_2 precipitated from the water, which in turn itself acts as a catalyzer. In fact, the fineness of the precipitate which envelopes it provides a more intimate contact between the catalyzer and the water than is possible with pyrolusite ore, which of necessity must be coarser to hold it in place. The pyrolusite is really a spark plug; the coke bed is the money-saver.

From the coke bed, the water passes into a sand-filter, which will remove all precipitated material not retained by the coke. It is a sure-catch for the iron. In no case will back-washing of the filter be as frequent as in sanitary filters. If precipitated manganese reaches the sand filters, it will in a short time coat the grains of the sand. Eventually these coated grains act as a catalyzer of manganese and iron, supplementing the work of the initial units through which manganese bicarbonate escaped unoxidized. In back-washing sand filters, these manganese coatings rub off readily and reduce the efficiency of these sands as catalyzers.

It has repeatedly been shown that iron and manganese can be completely removed; and in long periods, without exact proportioning of parts, with manganese reduced to as little as .02 to .04 p.p.m., it may be said that manganese is far below any danger point. This is in strong contrast with those who have written that all iron can not be removed if manganese is present; that all manganese can not be removed if iron is present; and so on.

If bacteria are a factor, or if they act only in an auxiliary capacity, they will have a chance to do their work on the bed of coke, which need not be cleansed for weeks or months. Bacteria need not be removed or killed, because they do not produce toxic substances nor are they toxic themselves.

Carbon dioxid liberated need only be afforded an opportunity for escape into the atmosphere.

The importance of hydrogen-ion concentration may have been over-emphasized by some advocates They may have underestimated the efficacy and the need of air. Atmosphere is always at hand and in plenty. Many tests were made and showed not more than 7.5 pH in the raw water (usually 7.3) and not more than 7.6 (usually 7.5) in the effluent from the filter.

A big advantage the proposed plant, or system, has is that it is self-regulatory and requires no close observation and manipulation to adjust it for varying amounts of manganese and iron in the source of supply. The human element is virtually eliminated, as when ore deposits are made.

Avoiding the use of lime prevents forming an undesirable coating on any of the material used, nor is the normal content of lime in the water raised. Lime is especially undesirable because it causes incrustation in boiler tubes.

In its final aspect the plant and procedure is a duplication of what transpires in the mains. In the mains the precipitated oxides do what the pyrolusite ore does in the plant. If bacteria are a precipitating agent in the mains, as to manganese their activity is principally initial; because once manganese oxides are formed they act quicker as precipitants than the bacteria and therefore do more work. But bacteria start the job. It is therefore not difficult to understand why, once a precipitate is formed, the

manganese in the raw water pumped into mains precipitates close to the pumping station and is absent in the water at a distance.

At this writing a plant for use in Brainerd is being prepared to operate early in 1932. In its essentials it will consist of the discharging of the water from the underground wells into a chamber containing pyrolusite of small size; then down a slide, exposing the water to the atmosphere, into a bed of special-sized coke of large surface area from which it will overflow into a regulation type of open sand-filter. Each unit will be equipped for backwashing or scouring to provide clean surfaces when needed. A diagrammatic presentation of the process and equipment is shown in Fig. 1.

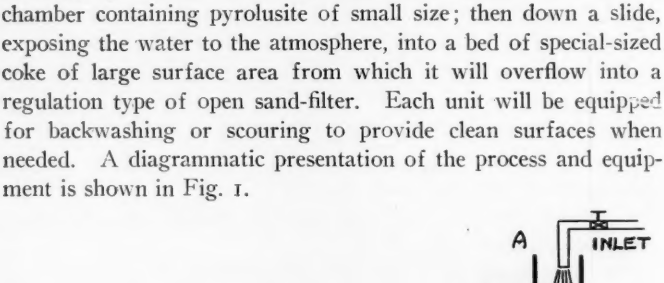

DIAGRAM OF UNITS USED
IN
ZAPFFE DEMANGANIZATION PROCESS

LEGEND

A - Catalyzing Chamber
B - Oxidizing Plane
Pyrolusite
Coke
C - Coke Box
D - Sand Filter
Sand & Gravel
Water

FIG. 1. Diagram showing units used in demanganization process.

No attempt will be made to eliminate bacteria; in fact their presence and aid will be encouraged because they are unquestionably an auxiliary and are in no sense detrimental. As to bacteria,

it may be said that they always have been and always will be present in the water; and if the plant operator becomes slovenly and permits iron and manganese to pass into the mains, the bacteria will report him. With what inexpensive device or better indicator of efficiency could a system be equipped?

III. CHEMISTRY.

Chemists have not been able to state definitely how the different elements found in water are combined. By the process of mathematics, iron and manganese are preponderantly shown to be combined with carbon dioxide as bicarbonates, $Fe(HCO_3)_2$ and $Mn(HCO_3)_2$, both of which substances occur as a solution only and never as a solid. Both are recognized as unstable salts which under proper conditions show strong affinity for oxygen.

Manganous salts are not so readily hydrolized as are ferrous salts. In neutral or weakly acid waters, atmospheric oxygen has no effect on the bicarbonate of manganese. Although acids dissolve iron hydrates, the hydrates will oxidize readily in the presence of air in neutral to weakly acid solutions. That is the first principle to be regarded.

L. Dieulafait,[2] in 1885, advanced the general principle that when one of several reactions takes place, the first to occur is that one which is attended by the greatest evolution of heat; consequently, if MnO and FeO are both present and CO_2 is available, then not only will manganese carbonate form first but will also be the more stable. Furthermore, if O and CO_2 act together in considerable excess, Fe_2O_3 and MnO_2 will be formed; but if they act slowly and are present in small quantities, then the oxygen will unite with the iron to form Fe_2O_3 and carbon dioxide will unite with the manganese to form $MnCO_3$, because in this instance the reaction with the iron generates the more heat, to wit:

(1) $FeO + CO_2 = FeCO_3 + 5.0$ calories
$MnO + CO_2 = MnCO_3 + 6.8$ "

(2) $2\,FeO + O = Fe_2O_3 + 26.6$ "
$2\,MnO + 2\,O = 2\,MnO_2 + 21.4$ "

[2] Compt. Rendu, vol. 101.

This illustrates the necessity of providing an excess of oxygen by some procedure to insure the formation of manganese dioxide. In the same regard, the presence of an excess of oxygen relegates the consideration of carbon dioxide to one of minor importance; that is, it is the wrong attack to center one's thoughts on the necessity of reducing the content of carbon dioxide in ground-water in order to extract manganese without providing for the addition of an excess amount of oxygen to satisfy both the iron and manganese in the formation of their respective insoluble oxides.

Iron and manganese compounds have many similarities, and for that reason many people apparently have viewed them as susceptible to the same treatment. Attempts based upon or governed by that view have led to failure. Although many similarities exist, the differences between the two are such as to make demanganization possible, provided manganese is made the objective.

The reaction for iron, as worked out by J. Tillmans in 1914, for alkaline and weakly acid solutions, is

$$2\ Fe(HCO_3)_2 + O + H_2O = 2\ Fe(OH)_3 + 4\ CO_2$$

Ferric hydroxide is a stable compound. If there is an intermediate stage of ferrous hydrate (which is not advanced), the oxygen in the water, or that in the air with which it may come in contact, will instantly produce the stable ferric hydrate. Ferrous hydroxide is not presented as a factor.

Although iron oxidizes easily, it must be remembered that in some waters other substances may be present that can retard oxidation and precipitation. Iron hydroxide can be held in a colloidal state. E. S. Moore and J. S. Maynard have lately worked extensively on this phase of the problem in connection with surface waters. Each case becomes a problem by itself.

In the case of manganese it is definitely known that manganous hydroxide forms, and only under favorable conditions can it be, as it must be, stabilized by the addition of free oxygen. $Mn(OH)_2$, like the bicarbonate form, is soluble in water. Tillmans gives the equation as follows:

$$Mn(HCO_3)_2 + 2\ H_2O \leftrightarrows Mn(OH)_2 + 2\ H_2CO_3$$

$Mn(OH)_2$, by the addition of oxygen, becomes $Mn(OH)_4$, and that in turn is further changed to a combination in which MnO_2, or other oxide forms, are a part. The reaction shown is a reversible reaction, and a control must be established or nothing results. We learn an interesting lesson from the work of Bradley, described by Zapffe in 1929. He developed a method of leaching manganese from iron and manganese-bearing rock formations, using ammonium sulphate as the leaching agent. By first roasting the ore, the manganese dioxide present was reduced to manganous oxide, which is quickly soluble in warm ammonium sulphate. Manganese sulphate and ammonia gas were formed in the leaching reaction, which was also found to be reversible and presented difficulties. To prevent the reaction from reversing itself in the presence of the generated ammonia gas, special physical conditions had to be provided. These were simple, but were, nevertheless, an innovation. High temperature and low hydraulic pressure were the regulators. The ammonia gas generated was exhausted and promptly used as a precipitant, to reform ammonium sulphate and manganese hydrate, to wit:

$$MnSO_4 + 2\ HN_3 + 2\ H_2O = (NH_4)_2SO_4 + Mn(OH)_2$$

But here was the unstable manganous hydroxide. This hydroxide had to be oxidized promptly to achieve the objective, therefore precipitation was provided for in chambers apart from the digesting chambers. When exhausting the newly formed ammonia gas from the digester, atmospheric air was also drawn into the precipitating chambers and a thorough mixture obtained under slight pressure. Thereby the affinity of manganous hydroxide for oxygen was satisfied and a stable though partly dehydrated manganic hydrate was formed, to wit:

$$2\ Mn(OH)_2 + O = 2\ MnO.OH + 2\ H_2O$$

or, as Tillmans puts it, $Mn(OH)_4$. Atmospheric oxygen does not act on manganous hydroxide in neutral or weakly acid solutions, but it oxidizes readily in alkaline solutions. Different views may be held as to how this alkalinity should be provided in demanganization of water; but it has been made apparent that the

degree of alkalinity needed is slight, and it may be fostered in a simple manner.

In 1914, when Tillmans first wrote, ozone had been used in previous experiments, but it proved to be too expensive a method. Tillmans stated that it was known that MnO_2 would precipitate manganese from waters as a hydrate, and he claimed that the oxygen of the water formed MnO_2 from the hydrate, the bicarbonate radicle being set free. Because the manganese dioxide that was formed coated the sand grains of the filter, he advised removing the iron first to prevent it from rendering ineffective these manganese coatings. Incidentally, Tillmans did not consider manganese difficult of removal if present as a sulphate, provided some bicarbonate was also present, and he stated that it rarely happens that some is not present. Some experimenters have held that manganese can not be removed if present as a sulphate. In laboratory work, however, manganese solutions are commonly made by using the sulphate.

Up to 1914 many conflicting ideas had been advanced and Tillman's ideas, to be found in several of his publications, show the general thought of that time. Tillmans did not dwell on CO_2, lime, or hydrogen-ion concentration, considered by so many subsequent writes as essential.

To give an idea how different the views of investigators have been, I present statements made by C. A. H. von Wolzogen Kühr, a chemist and bacteriologist of Amsterdam, Holland, writing as late as 1927. That writer concluded that, at Leiduin, bacteria of a lower order played an essential part in depositing manganese; but we are here interested in his views of the inorganic chemistry, which he deserts for the biochemical. He states that:

> The difficulty of oxidation of manganous bicarbonate by oxygen of the air was shown to be associated with the hydrogen-ion concentration in the solution.
>
> Tillmans' claim regarding manganese in alkaline solutions is untenable because hydrogen-ion concentration was not determined.
>
> Tillmans leaves biologic processes open, even though they may be but subordinate.
>
> Manganic oxide has the capacity to retain manganese as manganese

compounds from watery solutions. MnO_2 is regenerated by the additions of muds precipitated.

He found brown manganese oxide, formed by micro-organisms, lying in their cells; and that they operate in both alkaline and acid waters, in a range of pH from 5 to 11.

In anærobic processes undissolved manganic compounds can pass into dissolved ones, and that manganous compounds can be transferred into undissolved manganic compounds.

He proposed adding a surplus of alkalai, then an agent of oxidation and then MnO_2.

Test with air pumped into water for hours failed to deposit manganese when pH was 8.8 to 9.6 but would result if pH were 10.

He found: ". . . the problem is entirely of a microbiological nature."

H. P. Corson, writing in 1916, made a thorough study of the subject. River waters in southeastern Illinois were impounded for use at a hospital and filtered for sanitary purposes. The containers and the filter sands after long usage became covered with a black precipitate which analysis showed contained manganese. The surface waters contained only about 0.1 to 0.2 p.p.m. manganese. In his tests Corson dissolved manganese sulphate to obtain water containing manganese. It should be noted that Corson worked with manganese in solution as a sulphate, which several investigators considered an obstacle to removal of the manganese. The statements made by Corson and considered pertinent to the problem at hand are:

When manganese-bearing water is filtered through manganese permutit the manganese in the water is removed by the formation of a lower oxide of manganese by reaction between the manganese in the water and the manganese dioxide in the substance used.

Manganese is added to the permutit by the manganese removed from the water. The manganese dioxide increases and the filter medium approaches in composition pure manganese dioxide with each successive regeneration and reduction.

The deposit on sand eventually removes manganese. It is catalysis by manganese dioxide assisted by direct oxidation by the dissolved oxygen. Oxygen evidently oxidizes the lower oxide of manganese to dioxide at the time the manganese is removed. The process is therefore catalytic and no regeneration is necessary.

The lower the content of free carbon dioxide and the higher the content of bicarbonate, the lower will be the hydrogen-ion concentration, and therefore the greater the tendency toward the precipitation of manganese.

Removal of manganese had not then become popular and nothing, we might say, was made of those ideas in the furtherance of work to devise a practical process.

R. Schmeitzner, a German engineer, writing in 1913, discussed demanganization and designated the use of lime and permanganate too clumsy and too costly a method. He credited the Chief Chemist of the Egyptian government with being the first to make demanganization appear reliable and practical. The process depended on contact with pyrolusite, and he said that "the manganese in the water was oxidized to MnO_2 and as such promply deposited upon the pyrolusite, being drawn to the latter like iron to a magnet." Schmeitzner said that a plant had not been built, but hinted that the process would be tested for use in Dresden. This was prior to Tillmans' work. One would be led to believe that the pyrolusite was to be used somewhat as a filter medium.

Earlier experimenters made no definite statements regarding the nature of the phenomenon and alluded vaguely to one thing or another, but Corson is clear in his conclusion that the phenomenon is catalysis. To explain this it may be said that the mere contact of $Mn(HCO_3)_2$ with MnO_2 produces $Mn(OH)_2$ from the bicarbonate and leaves the dioxide unchanged—as was found in the Brainerd tests, after two years of usage. Surface tension and adsorption are terms often used to designate the phenomenon called catalysis. The action is difficult to diagnose. A force possessed by MnO_2, not definitely isolated as yet but possibly electronic in nature, causes a disruption of $Mn(HCO_3)_2$, producing $Mn(OH)_2$ and 2 CO_2, without the MnO_2 molecule being in any way affected by the disruption which the bicarbonate molecule suffers. That is why the pyrolusite used in this process has an indefinite life. It may be rendered less effective if the grains should become enveloped with slimes of other substances precipitated from the water and themselves not possessing catalytic

powers. Scrubbing by flushing with clean water, when so needed, will restore the pyrolusite to its full effectiveness. That in itself is suggestive that the surface of the catalyst is an important feature, or that catalysis is a phenomenon exhibiting itself only at the surface. The principal substances precipitated on the pyrolusite were oxides of iron and manganese. Because elements that form a series of oxides invariably stimulate catalytic oxidation, the pyrolusite actually in time becomes more powerful, probably up to a certain point of activation, due to the addition of the ferric oxides. Precipitated manganese on the inert basic coke, which acts as a support, is a well recognized method of promoting the power of the catalyst. When these precipitated oxides became the hosts of bacteria, enzymes produced by the latter also add to the catalytic powers. It is very clear then, that in a practical operation it is impossible to proceed without giving due recognition to both the organic and inorganic agencies and their processes and all the energizing forces that they contribute. Here is nature at its best, yet so simple.

IV. APPLICATION TO GEOLOGY.

Throughout this study several matters are apparent that bear directly on the solution, transportation and deposition of manganese from surface waters. Deposition of manganese is different from that of iron because the bicarbonate of the former does not oxidize during exposure to atmosphere as iron bicarbonate does, and the required conditions as to alkalinity or acidity differ slightly.

Lakes and seas, bays, gulfs, or similarly enclosed bodies in which sedimentary deposits containing iron and manganese form, are from all practical considerations not different than open wells or storage reservoirs or settling basins of a water system. At the bottom of the Brainerd wells and reservoirs a large amount of precipitate, yellowish to brown in color, always accumulates. That not all of the iron and manganese in city waters is precipitated in the various storage basins is solely a matter of not having provided the proper conditions for all parts of the body of

water therein contained. And so it should be found as to lakes, bays, etc.

Surface waters have been represented repeatedly as being lower in manganese than underground waters. We may well ask: To what extent is that correct? We are confronted first by an insufficiency of analyses, due largely to so little attention having been given to manganese in waters of any origin; and, next, an insufficiency of complete sampling. In ground waters, manganese was hardly known prior to 1906, and such waters were seldom analyzed for manganese before 1915, only 16 years ago; therefore, we do not know what value to place on a statement as to content even in ground waters.

When sampling surface streams, it is necessary to test the water at the source of the stream, which would be a spring of underground origin; and at various places toward its mouth, because progressively manganese should be less due to catalysis en route. When sampling lakes, it is essential to gather samples at various places over the surface and at different depths, because different bacteria want different conditions of light, organic matter, oxygen and currents of waters. It is not a small task to sample and meet those many conditions. Sampling city water at taps in homes, similarly, is useless in most cases.

Underground waters presumably obtain their manganese from the rock materials through which they flow, and when they issue as springs or in wells, they are still in the stage of adding to their manganese load. As surface waters, they meet with all sorts of conditions; and all sorts of agencies are operative, either extracting the manganese or supporting retention. The soil and the surfaces of rock outcrops are abundantly supplied with bacteria; one of the thread bacteria is a manganese-soil-bacteria. All aid in various ways in causing rock-decay. Some are efficient in attacking manganese-compounds. Surface waters are simultaneously dissolving soluble manganese salts. If the rates of flow are slow, the condition of detention or contact is filled satisfactorily for catalysis and subsequent deposition of oxides.

Manganese is, therefore, found in widely differing quantities

in different localities, situations, and depths. The lowest content occurs in the surficial layers of bodies of water, and places where the oxygen-content is sufficient. Rapids and water-falls are natural ærating devices. Precipitated iron hydroxides settle quite fast if coagulation is fostered. Natural coagulants are numerous. All the conditions in Brainerd water mains or in the plant provided for the demanganization of the Brainerd water are present in streams and lakes, and in these manganese can be continually in process of deposition.

In open waters, especially in shallow waters standing quietly and in deep waters where quiet conditions can exist at depth, also with darkness prevalent, conditions are again comparable to certain parts and conditions of a municipal distribution system. That is to say, that which is ascribed to biochemical action in water-distribution systems of municipalities has its exact counterpart in streams, ponds, lakes and seas. Time and again the writer has observed manganese and iron deposited by bacteria in the waters standing in idle open pits and in certain cross cuts and drifts in underground mines (of the Cuyuna Iron Ore District) near Brainerd, where the process proceeds before one's eyes.

The fact that we may be dealing with so small a quantity as one part per million, and often less than that, is not even a factor. It has been sufficiently demonstrated that during the past ten years Brainerd well-waters have brought to the surface daily not less than 0.8 p.p.m., which amounts to one ton of metallic manganese or about 1–1/3 tons of oxide precipitate per year. Geologic periods are measured by hundreds of thousands of years; and if, as occurred at Breslau in Germany, Cheltenham in England, and numerous other places in Europe, excessive amounts of iron and manganese were contributed in exceedingly short periods, it is not difficult to conceive the building up of large thickness of oxides of manganese and iron. There is here a strong argument for the sufficiency of ordinary weathering as the source of manganese. The need of contribution by igneous magmas may heretofore easily have been over-emphasized.

After about ninety years of observations of thread bacteria,

enough is now known about these organisms to state that the great variations in environment under which life exists, and the great variations in the kind of salts of iron and manganese present in water, provide suitable conditions nearly always for one or the other of these important micro-organisms. Inasmuch as two of these organisms, *Crenothrix polyspora* (Cohn) and *Leptothrix ochracea* (Kützing), are both the most common species and the best depositors of manganese, manganese may be expected to be continually in process of precipitation. Once the hydroxide of manganese is formed by bacteria, if oxygen is available to convert it into manganese dioxide, the latter by its presence speeds up and makes more thorough the deposition of the manganese in solution. Two agents of depositions, the one biochemical and the other inorganic in character, are operating at the same time. Only simple conditions or environments are needed for precipitation. It is a simple phenomenon, though it may seem puzzling.

A condition that must be fulfilled to complete the process is slight alkalinity, but as to other conditions little else is required. Some students place great importance on the need of a low content of uncombined CO_2; some advocate introducing lime; some advocate values of 8.5 to 10 or more of hydrogen-ion concentration; and so on. In their purposes these several things are closely alike, if not the same. In a plant it is a matter of which of these steps is the simplest and easiest to operate and control, whereas in lakes or other bodies of water it is a case of several conditions possibly existing at the same time and thereby insuring or expediting deposition.

The Brainerd tests showed that the water had a pH of about 7.3 before it entered the chamber containing the pyrolusite, about 7.4 when it entered the filter and about 7.5 after it had passed through the filter. This is an indication of very low alkalinity. In lakes or seas lime-secreting organisms and plants can produce the required degree of alkalinity. Streams feeding such bodies of water do not always contribute enough lime. In special cases, deposits of manganese and iron rest on limestone, and the presence

of lime in the water surely continued long after deposition of the lime beds. In other instances, basic lava-flows into seas would be a favorable factor. Associating them with ore-deposition requires only their action in the rôle of precipitants. Experimenters in Germany advocated the use of crushed lava in plants designed for the removal of iron and manganese. Porous lavas would act like the coke-beds.

The extent to which the content of manganese in water is affected by the presence of organic matter has apparently never been investigated. The subject is worthy of investigation because of the recent work by Moore and Maynard, in Canada, regarding the solution, transportation and precipitation of iron and silica in surface waters. Moore and Maynard showed that iron is carried as bicarbonate in natural surface solutions high in organic matter, but in all probability is transported as a ferric hydrosol stabilized by organic colloids, and that as much as 36 p.p.m. ferric oxide, formed by the oxidation and hydrolysis of ferrous bicarbonate, can be held in colloidal solution by 16 p.p.m. organic matter. Perhaps something of a similar kind applies to manganese; it would help to account for large contributions of manganese salts to seas, where the deposition of the oxides and hydroxides could then occur as already outlined.

Geologists have little opportunity for conducting investigations of such problems as the one described. Although the occasion for the investigation was created by conditions existing in a municipal water supply, it is manifest that agencies have there been operating in a natural way and unaffected by artificial manipulations. For the conditions ascertained, exact counterparts may be found in large open bodies of water, or within a formation itself, in which deposition may take place uninterruptedly by identical processes. To that extent these Brainerd tests should be of value and provide answers to many questions involving deposition of manganese by catalysis and by bacteria in formations of sedimentary origin. They also indicate how a minute grain of any substance becoming coated with manganese-

dioxide can become the nucleus of concretions and foster their growth. Bacterial casts and slimes are nature's glue.

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VARIETIES OF CHROMITE DEPOSITS.

EDWARD SAMPSON.

That chromite may form at a late stage in magmatic differentiation has been pointed out lately,[1] but this view is not as yet generally accepted, as I gather by general discussion and by published comments.[2]

This note presents some new evidence for late chromite-forming solutions and advocates a classification of chromite occurrences into three rather sharply defined groups.

In the past two years I have examined a number of chromite deposits, and have searched for specimens which might carry conviction to those who doubt the occurrence of hydrothermal chromite. A number of these specimens are here illustrated with the hope that, independent of other lines of evidence, they will prove conclusively that chromite may occur as a hydrothermal mineral. It still remains to be shown how much chromite is hydrothermal, even in the deposits where some of the chromite is demonstrably of this origin; but the qualitative fact should be established first, and the illustrations herewith are offered for that purpose.

A field and laboratory study of a number of chromite occurrences suggests a somewhat tentative classification into three rather distinct groups. This classification is proposed, fully realizing that at present it is not possible to assign many deposits to any one of the groups; but I believe that if such a classification be kept in mind during the examination of deposits, valuable

[1] Sampson, Edward: May Chromite Crystallize Late? ECON. GEOL., vol. 24, pp. 632–641, 1929.

Ross, C. S.: Is Chromite always a Magmatic Segregation Product? Idem., pp. 641–645.

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observations may be made. This classification is essentially like that of Fisher.[3]

The three proposed classes of chromite occurrences are as follows. First: chromite formed earlier than olivine or contemporaneously with it and in part included in olivine grains. Second: chromite formed at a late magmatic stage and crystallizing with the last truly magmatic silicate, commonly either bronzite or plagioclase. Third: chromite formed from hydrothermal solutions, for the most part immediately preceding or contemporaneous with intense serpentinization.

The first class of chromite occurrence has been thought to be of wide distribution, but close study seems to remove many deposits from this class. Indeed, it would now seem that chromite formed at an early magmatic stage does not occur in sufficient concentration to form ore. Where chromite does occur in workable concentration, it appears that some process other than the unmodified accumulation of early-formed crystals has been effective. In accord with this conclusion is a suggestion by A. F. Buddington,[4] that the complete absence of chromite as inclusions in basaltic lavas and basic dikes, in spite of the not uncommon inclusions of olivine nodules, is fair evidence that chromite concentrations do not form at an early magmatic stage.

The most certainly established case of early chromite of which I know is that of the peridotite dikes of Skye recently described by Bowen.[5] Diller[6] gave strong reasons for regarding the deposit of the Castle Crag mine near Dunsmuir, California, as early magmatic; but Fisher has cast some doubt as to the certainty of this conclusion.

The second class of occurrence is typified by the deposits of the Bushveld.[7] In this type chromite is associated with pyroxen-

[3] Fisher, L. W.: *op. cit.*, p. 692.

[4] In personal conversation.

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[6] Diller, J. S.: Chromite in the Klamath Mountains, California and Oregon. U. S. Geol. Survey Bull. 725, pp. 21–22, 1921.

[7] Wagner, P. A.: The Chromite of the Bushveld Igneous Complex. So. African Jour. Sci., vol. 20, pp. 223–236, 1923.

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ite rather than with dunite, and the chromite is commonly intimately intergrown with poikilitic bronzite and not uncommonly with plagioclase. The type of differentiation producing bronzitite, norite, and anorthosite appears to be particularly favorable. Serpentinization is not intimately associated with the ore-forming process. Examples of this class are the ores of the Bushveld igneous complex of the Transvaal, the "Great Dike" of Southern Rhodesia, and the Stillwater-Boulder belt of the Beartooth Mountains of Montana. Verner Jones [8] has recently described a deposit near Sheridan, Montana, which appears also to be of the late magmatic class. Here the chromite lies in, and is genetically associated with, diorite, the ore itself being an intergrowth of chromite and hornblende.

In the late magmatic type of deposit, a type of structure in which minute chromite octahedra form branching chains of crystals contained poikilitically in a silicate crystal is common.[9] This type of structure is illustrated in Fig. 1.

The third class, namely hydrothermal, is widespread; though in a deposit where evidence of hydrothermal origin can be secured, it is not yet possible to establish whether the whole deposit is of this nature. The evidence consists of impregnations and veins closely associated with serpentinization, and commonly showing active replacement by chromite. Localities from which strong evidence has been secured are: the offset deposits in conglomerate at Selukwe [10]; Kraubat, Styria [11]; Wood's Mine, Pennsylvania [12] (Figs. 2 and 3); Martin claims, Hell Roaring Creek, near Red

Eastern Transvaal. XV Internat. Geol. Cong. Guide Book to Excursion C–19.

Sampson, Edward: Magmatic Chromite Deposits in Southern Africa. In press.

[8] Jones, Verner: Chromite Deposits near Sheridan, Montana. ECON. GEOL., vol. 26, pp. 625–629, 1931.

[9] Sampson, Edward: Magmatic Chromite Deposits in Southern Africa. In press.

[10] Sampson, Edward: May Chromite Crystallize Late? ECON. GEOL., vol. 24, pp. 633–635, 640, 1929. Discussion, The Origin of Chromite. *Idem*, vol. 26, pp. 662–669, 1931.

[11] Sampson, Edward: May Chromite Crystallize Late? *Idem*, vol. 24, pp. 635–636.

[12] *Idem*, pp. 633, 640.

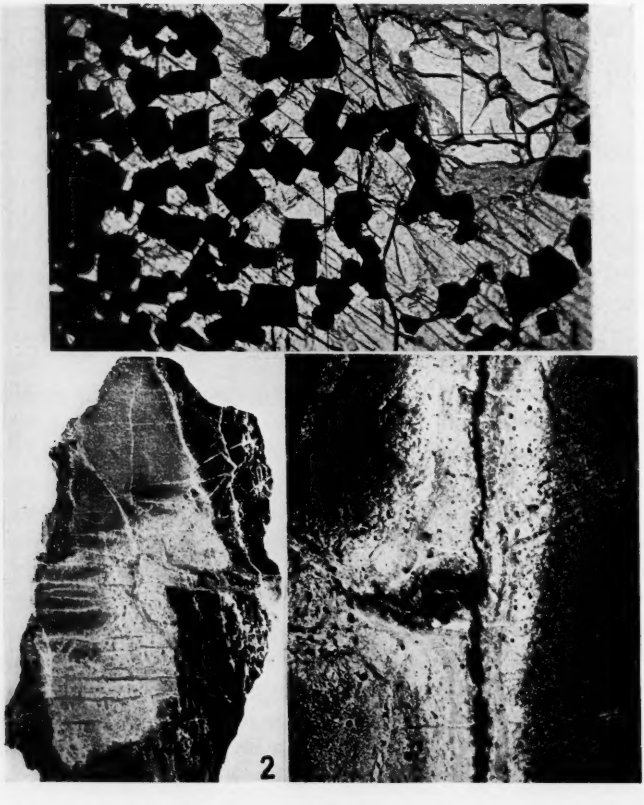

FIG. 1 (above). Chromite with chain structure in single crystal of bronzite. Olivine grain partly altered to serpentine, in upper right. Nodule of the chromitite which forms the chrome ore. Lala Panzi, Rhodesia. × 48.

FIG. 2. Veins of chromite branching from main feeding vein at left and including serpentinized rock. Wood's mine, Lancaster Co., Penn. × 0.5.

FIG. 3. Vein of chromite bordered by intense serpentinization, and evenly disseminated chromite crystals. Wood's mine, Lancaster Co., Penn. × 0.9.

Lodge, Montana (Figs. 4 and 5); and the Old Dominion pit, Thetford Mines, Quebec (Fig. 6).

Another group of deposits should also be mentioned, namely, those in which chromite is in close association with diopside or tremolite, or such silicates. Although the occurrence of these minerals is not uncommon, no adequate description is available of a deposit in which these minerals are conspicuous. However, C. S. Ross [13] has pointed out the highly significant presence of minor amounts of these minerals associated with chromite in the dunites of North Carolina. For the present, it would seem best to place the deposits associated with diopside or tremolite in the hydrothermal class although when we know more about them it may be desirable to put them in a class by themselves.

In conclusion, it is appropriate to consider the behavior of other members of the spinel group. True spinel ($MgO.Al_2O_3$) commonly forms by contact metamorphism in limestone under conditions implying substantial migration and extreme mobility of the material, with mineralizers playing an important part. Gahnite ($ZnO.Al_2O_3$) has been found by Ross [14] to be a widespread minor constituent in the replacement and vein deposits important for iron and copper sulphides in the Southern Appalachians. The gahnite formed at an early stage characterized by ferromagnesian minerals. Magnetite ($FeO.Fe_2O_3$) commonly forms as replacement deposits by a residual solution genetically related to granite pegmatite. In such deposits the replacement by magnetite has clearly been brought about by hydrothermal solutions.[15] Hercynite [16] ($(Fe, Mg)O.Al_2O_3$) occurs in the Peekskill, New York, region in association with corun-

[13] Ross, C. S.: Is Chromite Always a Hydrothermal Mineral? Econ. Geol., vol. 24, pp. 641–645, 1929. Discussion, The Origin of Chromite, Econ. Geol., vol. 26, pp. 540–545, 1931.

[14] Ross, C. S.: The Copper-bearing Pyrrhotite Deposits of the Southern Appalachians. U. S. Geol. Surv. Bull., in press.

[15] Colony, R. J.: Magnetite Iron Deposits of Southeastern New York. N. Y. State Museum Bull. 249 and 250, 1923.

Singewald, J. T., Jr.: Origin of Iron Ores of Iron Mountain and Pilot Knob, Missouri. Amer. Inst. Min. and Met. Eng. Trans., 1929, pp. 330–339.

[16] Rogers, G. S.: Geology of the Cortlandt Series and its Emery Deposits. Annals N. Y. Acad. Sci., vol. 21, p. 68, 1911.

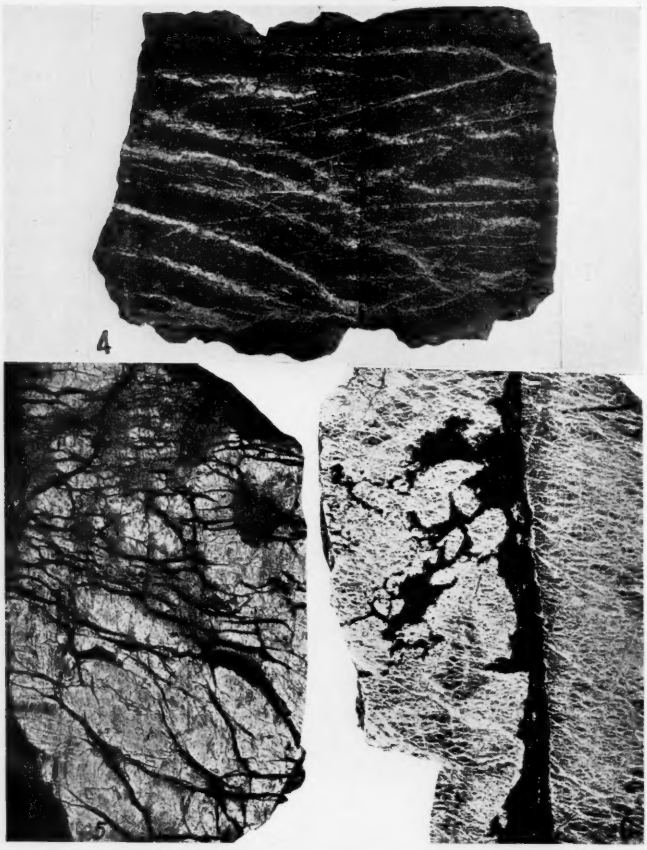

FIG. 4. Veinlets of chromite. Two faces of the specimen are polished and the photograph taken by reflected light which shows the chromite gray. West workings of Gallon Jug claim, Martin property, Hell Roaring Creek, near Red Lodge, Montana. × 1.0.

FIG. 5. Veinlets of chromite in serpentine vein on the face of the specimen. The chromite veinlets do not penetrate the body of the specimen. Location same as Fig. 4. × 0.37.

FIG. 6. Chromite replacing dunite which has been highly serpentinized. Old Dominion pit, Thetford mines, Quebec. × 0.5.

dum and magnetite, forming deposits of emery on the contact of basic members of the Cortlandt Series of igneous rocks with aluminous sediments. Gillson and Kania [17] have shown these deposits to have been formed by hydrothermal solutions, both by alteration of the sediment and by endomorphism of the igneous rock itself.

On the whole, the spinel group is characterized by high mobility, and it would seem that chromite has this feature in common with the other members.

PRINCETON UNIVERSITY,
PRINCETON, N. J.

[17] Gillson, J. L., and Kania, J. E. A.: Genesis of the Emery Deposits near Peekskill, N. Y. ECON. GEOL., vol. 25, pp. 506–527, 1930.

FISSURE VEIN AND LODE RELATIONS IN MICHIGAN COPPER DEPOSITS.[1]

T. M. BRODERICK.

THE PROBLEM.

Of the 8,234,342,001 lbs. of copper which have been produced in the Michigan Copper District to the close of 1929, 3,623,979,900 lbs. have come from one single ore body in the Calumet conglomerate. Practically all the remainder has come from ore bodies in amygdaloids, the principal producers having been the following:

Kearsarge amygdaloid	1,413,472,932 pounds
Pewabic amygdaloid	902,422,784 pounds
Baltic amygdaloid	967,625,138 pounds
Osceola amygdaloid	478,277,432 pounds
Isle Royale amygdaloid	254,632,779 pounds
Atlantic amygdaloid	142,840,804 pounds

The remainder, constituting 5.4 per cent. of the whole, has come from scattered deposits in amygdaloids, in conglomerates and in fissures. It is apparent, therefore, that the important ore bodies of the district have so far all been in the interbedded amygdaloids and one conglomerate. These are called the "lode" deposits. A large rich ore body such as the Calumet conglomerate satisfied at least three structural conditions. First, it had access

[1] Presented before the Society of Economic Geologists, Charlottesville meeting, April, 1930.

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This paper is the second one of a series which the writer hopes to publish, the first one being "Zoning in Michigan Copper Deposits and its Significance" (Econ. Geol., vol. 24, No. 2, March–April, 1929, and No. 3, May, 1929). The present paper will be more easily followed by those who have read the preceding one and who are familiar with the general features of the geology of the district as presented in "The Copper Deposits of Michigan," U. S. Geol. Surv. Prof. Paper 144, 1929, by B. S. Butler and W. S. Burbank.

to the source of copper-bearing solutions at depth (either directly or through channels leading from the source); second, it offered through-going permeability toward the surface or was a part of a system of openings offering such a channel; and third, its channel was sufficiently restricted so that the solutions were not dissipated, to produce a huge deposit of non-commercial grade. The amygdaloid ore bodies likewise show evidence of resulting from similar structural controls.

The ore bodies in the Calumet conglomerate and Pewabic amygdaloid have been followed downward from the outcrop for practically 10,000 feet and are being followed to still greater depths. This gives direct evidence that copper was deposited over a depth range of nearly two miles, measured along the lodes. Other evidence, such as the rate of change in the ratio of arsenic to copper in depth, indicates that conditions were favorable for copper deposition for two or more times that distance. This subject was treated in an earlier paper.[2]

That the coincidence of these necessary structural conditions in any one lode was rare is indicated by the fact that of the two to three hundred amygdaloids in the section, only six are so far known to carry ore bodies, and of the twenty to thirty sedimentary beds only one has commercial mineralization.

Prior to mineralization the formation was tilted to form the Lake Superior syncline, and cross folding also took place. Many fractures of varying size and persistence were formed by these movements. Many of the fractures are mineralized and although they contain the same minerals as the lodes, there are more extreme concentrations of the minerals in the fissures. Thus, masses of copper hundreds of tons in weight were formed in the fissures, likewise massive datolite, or chalcocite, or rare copper arsenides, all of which are more disseminated in the lodes. Although the great spectacular masses of copper of the earliest mines in the district were on fissures, few of these mines were profitable and all of them were almost insignificant in size compared with the great ore bodies in the lodes. The greatest of the productive fissures yielded as follows:

[2] Broderick, T. M.: *op. cit.*

Minnesota	61,315,000	pounds
Central	51,875,000	pounds
Cliff	39,772,000	pounds
Phoenix	17,032,000	pounds
Mass [3]	15,155,082	pounds

Many other fissure veins were explored and produced small amounts of copper. In fact so far as production is concerned, the list might be continued by naming those of smaller and smaller production, finally including the thousands and thousands of local gashes an eighth of an inch or less in thickness which carry a little copper in a calcite or prehnite gangue.

Even some of the largest of the fissure ore bodies are in apparently non-persistent fissures. Thus the Central fissure cannot be seen at all in the Greenstone (Fig. 7) and was only with great difficulty traced below the Kearsarge conglomerate in the bottom of the mine (the drifts and stopes below the Kearsarge conglomerate as shown in the figure are mostly on another fissure 260 feet away from the projection of the Central fissure). Likewise the Mass fissure, Ahmeek, can be traced for only about 1200 feet along its strike. On the other hand the great persistent fault zones, which presumably extend to considerable depths, are characteristically unmineralized.

Thus the simple conception of a few deep-rooted amygdaloid and conglomerate solution channels is complicated by the highly concentrated mineralization found in the fissures. The known fissure ore shoots all play out at shallow depths and the fissures themselves seem to be of a local non-persistent character hardly to be expected to extend several miles downward as do the lode channels.

The fissure ore shoots present a problem. Why, in a district where solution channels are mineralized to great depths, do these fissure ore shoots bottom at shallow depths with a type of mineralization still high up in the zonal range in which copper deposition occurs?

The best opportunity to study many of the fissures is in the

[3] Still being worked in the Ahmeek Mine in connection with the mining of the Kearsarge amygdaloid.

mines operating on the lode deposits, where certain close relationships between the mineralization of the fissures and that of the lodes seem to exist. It is but another step to regard all similar mineralized fissures as related to lode deposits instead of reaching down to great depths as independent solution channels, and if there are no known lodes in the vicinity, then to use the fissure mineralization as a guide in exploring for lode deposits that are not exposed.

The fissure veins will be classified and discussed in three groups according to their probable relationships to the lodes: (1) Feeding fissures; (2) Short-circuiting fissures; (3) Leakage fissures.

The Feeding Fissures (*Fig.* 1).—Feeding fissures are best de-

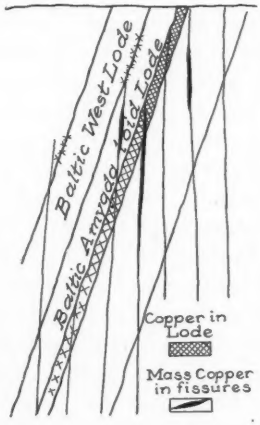

FIG. 1. Diagrammatic section showing relations of steep strike fissures and Baltic lode mineralization.

veloped in the mines on the Isle Royale and Baltic lodes. These lodes are mineralogically in the highest temperature zone that is being worked in the district. The lodes are fragmental amygdaloids and the characteristic gangue minerals are sericite and ankerite, besides the usual persistent minerals occurring throughout the entire zonal range represented in this district. The cop-

per is more highly arsenical and more chalcocite is present than in any of the other lodes. Abundant fissuring occurs with many of the most conspicuous ones in the footwall trap underlying the amygdaloids. The fissures strike at low angles with the lodes, and dip more steeply. They tend to swing into or follow along the lodes before crossing over into the hanging wall, although many of them disappear in the thick soft amygdaloids and do not extend into the hanging wall. These fissures carry the same minerals as are present in the lodes themselves, although chalcocite and ankerite are relatively more abundant in the fissures. More rarely bornite, chalcopyrite, specularite, and pyrite occur. Some contain important bodies of mass copper. Most of the mineralization in these fissures is in the footwall of the mineralized amygdaloid, although some of it occurs in the hanging wall. In many cases, especially in the Isle Royale mine, the copper in the lode itself seems to be associated with these footwall fissures, which suggests that the ascending ore-depositing solutions gained access to the Isle Royale and Baltic amygdaloids through these steeply dipping strike fissures. In places some of the solutions appear to have followed the fissures through the main Baltic lode and to have locally mineralized the first and even the more distant amygdaloids above, forming the so-called " West Lodes," one of which was an important source of copper in the Baltic mine.

The Short-Circuiting Fissures (*Fig. 2*).—The best known examples of this class are the fissures crossing the Kearsarge amygdaloid. The lode mineralization itself is of a lower temperature type than that of the Isle Royale and Baltic. These fissures, instead of striking nearly parallel with the lode, as in the case of the feeding fissures, are more nearly at right angles to the strike of the lode and almost vertical.

Although they are all practically identical in strike and dip, and in the fact that mineralization is rather closely restricted to their intersection with the lode, they differ widely in the type of mineralization. One of them has nearly the same mineralogical characteristics as the lode itself at the same elevation. It contains masses of native copper and a calcite gangue, and the

adjacent lode is chloritized for a short distance. The other fissures carry arsenides of copper, including domeykite, algodonite and whitneyite, with some nickel and cobalt arsenides, and some magnetite and specularite. The gangue is in most places quartz and dolomite, or ankerite. The adjacent lode is not only

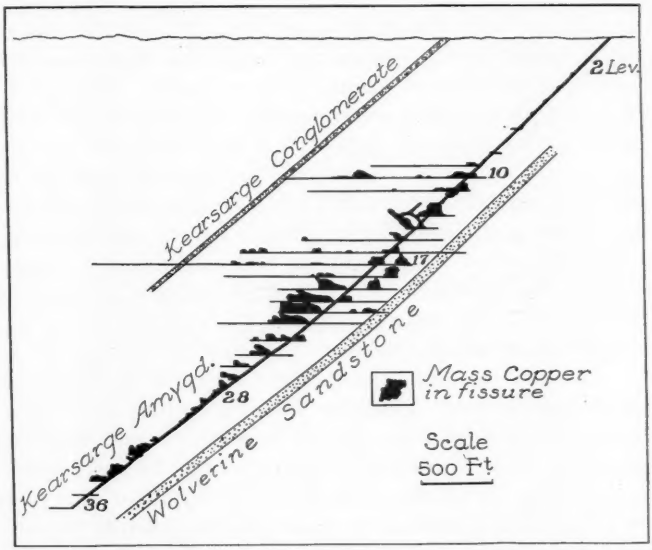

FIG. 2. Vertical section of Mass fissure and across Kearsarge amygdaloid lode showing distribution of known mass copper in fissure.

chloritized but sericitized. The one carrying mass copper belongs to about the same zone as the nearby lode itself, but the ones with arsenide belong to a much deeper zone. So far as is known, these fissures are not persistent along the strike. The Mass fissure splits up and turns into the bedding planes at about 250 feet in the footwall and 950 feet in the hanging wall of the Kearsarge amygdaloid. One of the strong arsenide fissures could not be found in an opening 2500 feet away from where it is strongly developed.

The explanation of the three types of mineralization, the amygdaloid copper, the mass copper on one fissure where it intersects the same amygdaloid, and copper arsenides with more deeply seated gangue minerals and associated rock alteration, on other fissures of the same system where they intersect the amygdaloid has been difficult. It has been considered, among other possibilities, that the solutions which mineralized the arsenide fissures came from some source separate and independent from those that mineralized the lode and the mass copper fissure. This is possible, although it requires some ingenuity to dispose of the coincidence of (first) arsenide deposition in the intersection with the same amygdaloid which (second) has native copper assumed to come from another source, and (third) the presence of still another fissure in the midst of the arsenide fissures and belonging to the same system, but mineralized with pure copper. Similar difficulties are encountered in attempting to explain the facts by assuming a different age and different type of solutions for the arsenide mineralization from that of the native metal mineralization. The idea that these fissures were feeders for the Kearsarge lode encounters several difficulties: first, that the minerals of most of them are different from the lode minerals; second, that one fissure, the Mass, is so different from the other fissures in mineralogy; third, that the lack of persistence along the strike is such that it is difficult to think of them as extending down to the considerable depths at which the source of the solutions is supposed to lie; and fourth, that they intersect other amygdaloids and also the Wolverine sandstone, which although less permeable than the Kearsarge amygdaloid, might be expected to have received some mineralization at least from the fissures if they were feeders. Hanging wall and footwall crosscuts and diamond drill holes have failed to disclose any ore bodies in the lodes near the Kearsarge ore body. Finally, the lode deposits, excepting the Isle Royale and Baltic lodes, seem to be independent of fissure feeders and to have themselves constituted the solution channelways to the depths so far mined. The Isle Royale and Baltic lodes are possible exceptions. They are in much deeper zones mineralogically and

the supposed feeding fissures, striking nearly parallel with the lodes and swinging into them from the footwall side because of their slightly steeper dip, are much more favorable structurally to function as such than the cross fissures intersecting the Kearsarge lode.

There is a simple explanation (Fig. 3) which avoids these

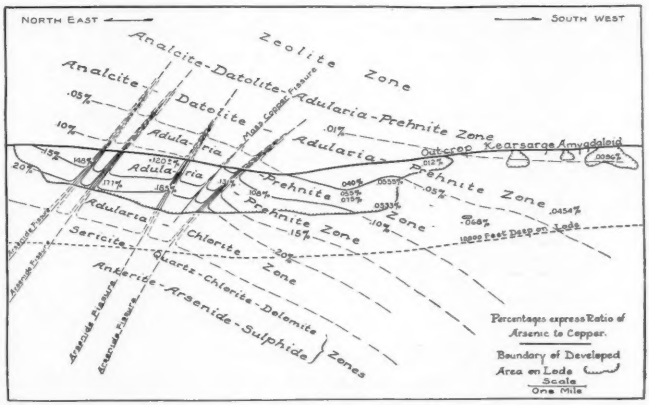

FIG. 3. Plan of Kearsarge amygdaloid lode showing short circuiting effect of cross fissures on mineral zones.

difficulties, and fits into the chemical, mineralogical and structural facts without apparent inconsistencies, namely, that both the Mass fissure and the arsenide fissures were mineralized by the Kearsarge lode solutions. The fissure lode intersections offered more open passages for a limited amount of the solutions ascending the Kearsarge lode. The arsenide fissures extended to greater depths than the Mass fissure and "short-circuited" the deeper seated type of solutions and thus caused the occurrence of the higher temperature type of minerals and wall rock alterations at abnormally high levels. These fissures did not rob the lode of any great part of its solutions, since the mineralization in the fissures remained near their intersections with the lode. They grade into another type which has conducted away more or less

of the lode solutions and which are therefore referred to as leakage fissures.

Leakage Fissures.—Any fissure that allowed the escape of a portion of the solutions moving upward along an amygdaloid or conglomerate may be called a leakage fissure. Practically every lode in the district had such leakages and they vary in size and importance. Many of the tight cooling joints in the hanging wall traps overlying the mineralized lodes have thin sheets of copper on them, and they constitute simple examples of this type of fissure (Fig. 4). More important are fissures like the one crossing the Pewabic lode which had mass copper mineralization thousands of feet in the hanging wall of the lode. Another example is the one persistent fissure crossing the Calumet conglomerate ore body, which yielded several tons of mass copper where intersected by a vertical shaft some thousands of feet in the hanging wall of the conglomerate. This gap between the mineralization in the lode and that in the leakage fissure is a feature common to both these examples and it may be present in most or all of the leakage fissures in the district.

Local Effects of Fissures on Lode Mineralization.—In many places in the Isle Royale mine the copper in the lode seems to be directly associated with feeding fissures, that is, the lode may be locally richer near the fissures. This enrichment near the fissures is said to be less noticeable in the Baltic lode, and at best it is rather intangible. However, the lode is not impoverished near the feeding fissures and is probably richer. On the other hand, the short-circuiting fissures have in numerous instances had the effect of diminishing the copper content of the lode in their vicinity. This is brought out by several kinds of evidence. The old reports of the mining companies commonly indicate it and old stope maps agree. In addition, our own observations and that of the mining men lead to the same conclusion. Why this should be is not fully understood, although several explanations are possible. Mineralizing solutions ascending the lodes found the fissure intersections especially easy to travel, and the advance wave of solutions reached a given elevation in the lode first near the

fissures. These solutions working out laterally into the lode used up much of the ferric oxide which seems to have been a necessary chemical agent in the precipitation of native copper. The parent lodes are chloritized near these short-circuiting fissures, indicat-

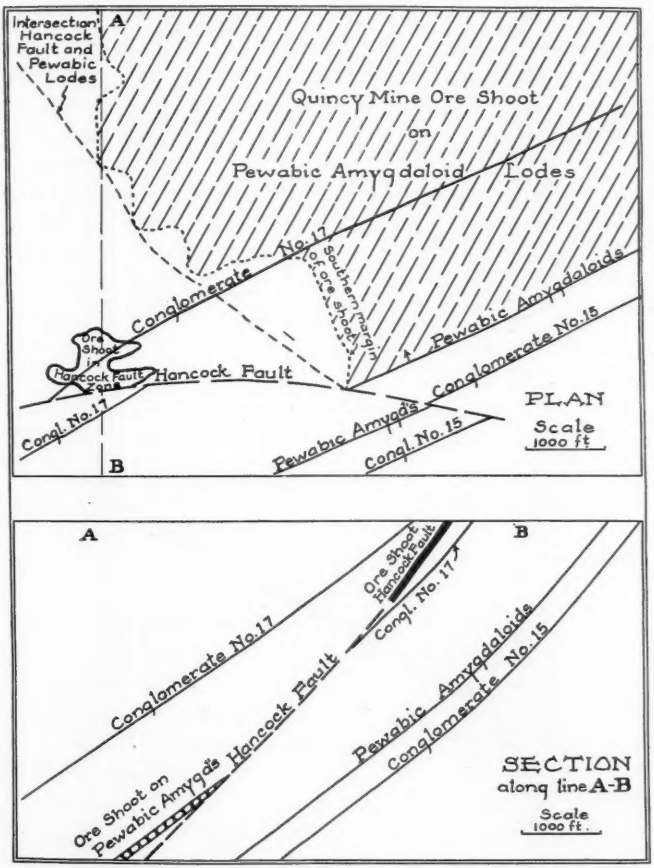

FIG. 4. Plan and section showing south end of Quincy mine ore shoot, and satellitic ore body in Hancock fault zone.

ing a reduction of the ferric iron to the ferrous state. The larger part of the metallic constituents of this first wave was deposited in the fissures at and near their intersections with the lode rather than in the lode itself. These early solutions likewise filled the openings in the lode with gangue minerals, chiefly calcite and chlorite. Therefore, the more slowly moving solutions ascending along the lode itself found the lode in the vicinity of the fissures already rendered unfavorable chemically and physically. A third explanation of diminished copper content near the fissures is that in some cases the fissures follow narrow bars of originally tight, brittle amygdaloid of a type originally unfavorable for mineralization. This is particularly true in the Kearsarge lode. Although the opportunity for direct observation of the effect of the leakage fissures on the feeding-lode mineralization has been limited, it seems that the feeding lodes are lower in their copper content near the intersections with the fissures.

Summary (Fig. 5).—Thus, by a study of the major lode de-

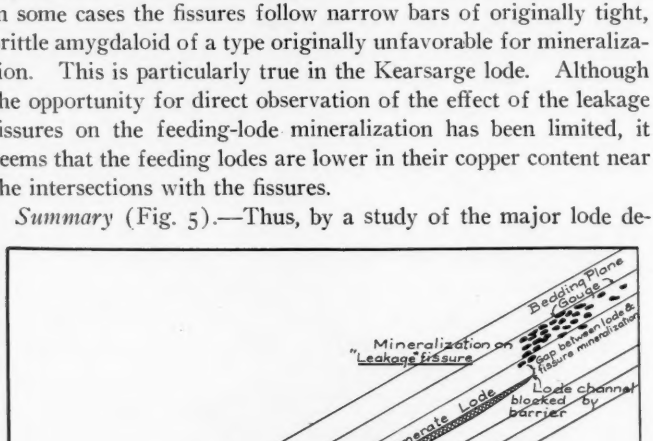

FIG. 5. Hypothetical composite section showing relations between lode deposit and the various types of fissures.

posits we recognize fissures that can be divided into three classes, according to their relationships to the lodes. There are those that are nearly parallel to the lodes in strike but somewhat steeper in dip, which seem to have brought mineralizing solutions from somewhere deep in the footwall into the lodes. The important examples of these feeding fissures occur in the zones of higher temperature mineralization. There are cross fissures whose intersections with the lodes apparently extended to considerable depths and formed easy channels for mineralizing solutions ascending the lodes. They brought deep-seated types of minerals and wall rock alteration into abnormally high environment, but did not conduct solutions away from the lodes to any great extent. They are termed short-circuiting fissures and the nearby lode is somewhat below normal in copper content. Finally there are the leakage fissures which allowed some of the solutions from the lodes to escape into the hanging wall where in some cases after travelling thousands of feet their copper was deposited. The lode near these fissures also is below normal in copper content. Fig. 5 is a hypothetical diagram showing what is thought to be the relationship of the mineralization on these three types of fissures to that of a major lode. The short-circuiting and leakage fissures lie in the plane of the diagram, and the feeding fissures and the lodes are at right angles to it.

APPLICATION.

The recognition of such relationships of fissure vein and lode mineralization may be of great importance in the exploration for new lode deposits. If we can recognize certain fissure deposits as having characteristics similar to those of fissures that seem to be of the leakage type, they can be used as starting points from which to work in searching for unknown lodes to which they may bear a similar relationship.

There is no known amygdaloid or conglomerate ore body that fails to reach the present rock surface. Structural conditions are such, however, that some of the ore bodies may not have extended more than one or two thousand feet above the present surface.

The Calumet conglomerate is the best example of such a possibility. For many miles this sedimentary horizon is known as a thin shaly or sandy layer, in many places but an inch or less in thickness, lying in the midst of a series of lava flows. At Calumet it rather abruptly opens out into a fairly coarse conglomerate up to twenty feet or more in thickness. This conglomeratic phase is only about six thousand feet long at the outcrop, and is divided along the strike into two major parts by an island of the thinner shaly phase. This conglomerate body becomes thicker and longer in depth and forms the host rock for the most productive body of copper mineralization so far known in the district. It apparently fulfilled the structural requirements to make it such in an ideal manner. It had access to the copper-bearing solutions, it had a high degree of permeability as compared with the surrounding rock, and it was sufficiently restricted so that the mineralization was not dissipated over too large a volume of rock. In this case the barrier confining the solutions was the tight shaly phase forming the edges of the thicker conglomerate phase which itself becomes shorter along the strike and thinner toward the surface. If this tendency continued in the eroded portion above the present surface, it is not unlikely that the conglomeratic phase was practically lacking within one or two thousand feet (Fig. 6). Thus,

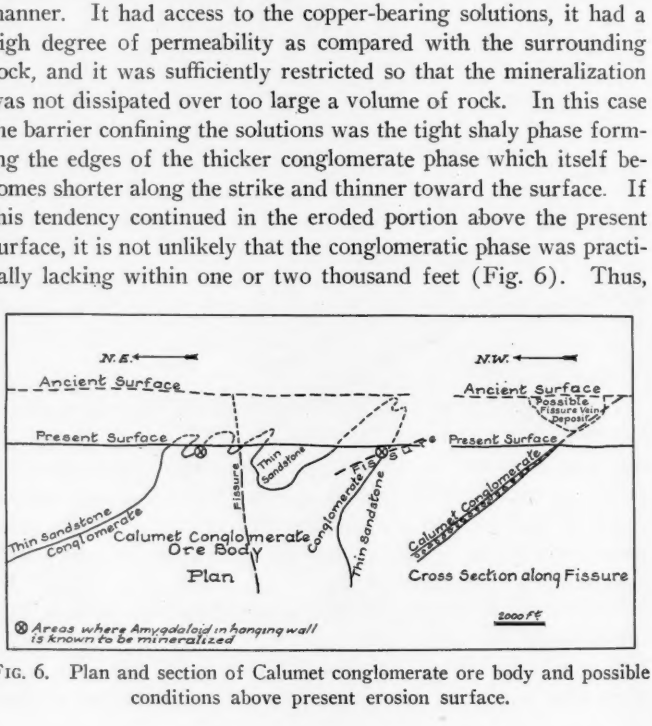

FIG. 6. Plan and section of Calumet conglomerate ore body and possible conditions above present erosion surface.

the conglomerate ore body would not outcrop on any surface above that point, and the Calumet conglomerate horizon at Calumet would be much as it is where known elsewhere for many miles—a thin, relatively impermeable shale. The question then arises as to how the solutions that mineralized the conglomerate could have made their escape, since that would be essential in providing opportunity for the enormous volume of solutions to travel through the lode. There are some hints as to how this was accomplished. At several places near the surface, there is a mineralization in the first amygdaloid in the hanging wall of the conglomerate. This amygdaloid is at the top of a thin flow and occurs from a few feet up to thirty or forty feet from the top of the conglomerate. At the very south end of the conglomerate ore body, at the surface, heavy copper mineralization was found in this amygdaloid, and the statement was made in old reports that this hanging-wall amygdaloid mineralization was connected with the conglomerate mineralization by continuous copper along a cross fissure zone. This is clearly a case where the solutions ascending along the conglomerate encountered a barrier condition in the conglomerate and in part at least escaped into the hanging wall along a fissure. There are other instances of escape into the hanging wall where the conglomerate thins out, and if that tendency to become less permeable extended upward into the eroded ground above the present outcrop, the tendency for the solutions to take advantage of every opportunity to escape into the hanging wall would increase. Finally, if carried to the extreme, the conglomerate at a certain distance above the present surface may have been completely closed off and the course of the solutions above that point would have been along any available fissures in the hanging wall. Fig. 6 shows what might very well have been the surface expression of the mineralization which in greater depth is the Calumet conglomerate ore body. There would be perhaps several mass copper fissure-vein deposits, and judging from conditions elsewhere, as in the Quincy-Hancock area where fissures have conducted away some lode solutions, the fissure mineralization might not extend down to the junction with the

lode channel, there being possibly a gap of many hundreds of feet in commercial copper above the junction.

Cross fissures that carry notable amounts of copper would therefore seem worthy of careful study to see whether or not their occurrence is such that they may be leakages from some unknown amygdaloid or conglomerate channelway, which may or may not be cut off from the rock surface by barriers. Of

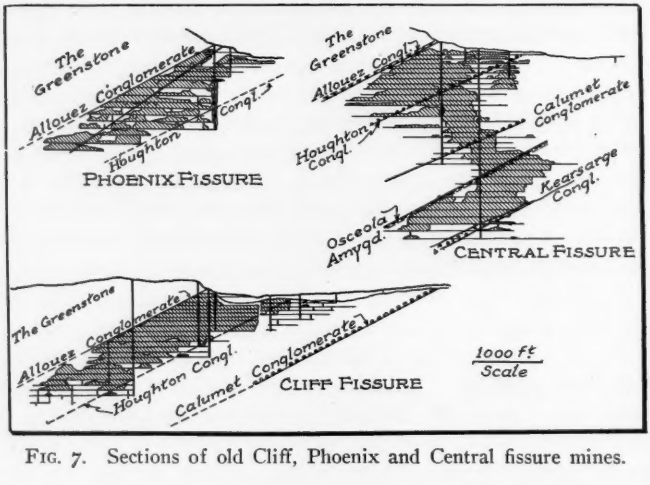

FIG. 7. Sections of old Cliff, Phoenix and Central fissure mines.

particular interest are the abandoned fissure mines of Keweenaw County, which were among the first deposits worked in the district. From the old Cliff mine to the old Delaware mine in Keweenaw County there is a stretch of 12 miles where the copper mined came almost entirely from fissures. In this area there are no known commercial amygdaloid or conglomerate deposits, but underneath a gougy sedimentary horizon at the bottom of the thickest flow in the district the famous old Cliff, Central and Phoenix mass copper fissures were found (Fig. 7). They are nearly vertical and about at right angles to the strike of the lavas and conglomerates. These fissures were for a time important sources of copper in the district. The Central shut down in 1898,

the Cliff and Phoenix about 15 years earlier. The mass copper gave out, although from descriptions of the mineralization and examinations of the old dumps, it was apparent that the bottoms of the old mines were still high up in the zonal range of copper deposition. It was a favorite saying among mining men that this area was not to be expected to carry lode deposits because the fissures got all the copper. Perhaps that may prove to be true. but the fissure deposits with their small but concentrated mineralization are in such contrast with the great lode deposits further south that the matter cannot be so easily disposed of. The realization of the fissure-lode relations just brought out, and the zoning studies indicating that the giving out of fissure copper in the old mines did not mean that the bottom of the copper zone was reached, lead to the serious consideration of the possibility that these are examples of the leakage fissures and that therefore a search for the feeding lodes would constitute a compelling exploration. Inspection of the section along the Central fissure reveals an almost ideal case, the fissure mineralization practically bottoming where the Kearsarge conglomerate is reached and the Kearsarge conglomerate there being shut off upward by a barrier of the same type as that which is present in the Calumet conglomerate; that is, it turns into a thin sandstone or shaly sandstone up the dip from that point. The question is whether or not the Kearsage conglomerate is the parent lode and the Central fissure the leakage deposit. The conglomerate contained some copper near the fissure and several stopes were opened on it. It may be that there is a lean zone in the conglomerate adjacent to the fissure and that drifting out along the conglomerate a few hundred feet would have disclosed important mineralization. The shaft is 2640 feet deep and its unwatering and recovery would necessitate a large expenditure.

It was decided to try out these principles underground by unwatering the Cliff and Phoenix fissure mines which were about 1500 feet in depth. No specific horizon, such as the Kearsarge conglomerate at Central, is indicated as a possible parent lode. The gap that exists between the mineralization in a leakage fis-

sure and the parent lode is present in these old fissures, and is of unknown extent. The method of exploration is to start on the bottom levels of the old mines and crosscut the formations, working farther away from the old deposits both horizontally and vertically. So far nothing has been observed in the old workings and at the bottoms of the old mines which makes the underlying idea seem inapplicable at these particular places. The fissures, although they are not well mineralized with copper in the bottom levels, are of good thickness and filled with calcite, prehnite and epidote, which is a mineral combination characteristic of the upper part of the copper zone. Had they turned into the quartz-ankerite-chalcocite or -arsenide fissures that are characteristic of the lower parts of the copper zone, the project would have appeared less encouraging. Another significant feature is that on level after level throughout these old fissure mines, the wall rock has been examined, and the amygdaloids adjacent to the fissures are in every instance unaltered. This is a characteristic of the upper part of the copper zone; the lower parts show sericitization and chloritization of the rock adjacent to the fissures. There is not even the bleaching of the amygdaloids which characterizes the intermediate zones. Therefore, it seems unlikely indeed that the copper gave out because of too high a temperature. The chief elements of uncertainty in the exploration are whether these fissures may not be so persistent in depth that they made direct connection with solution sources, thus being independent of any amygdaloid or conglomerate channelway, or on the other hand, if they are leakages from a lode channelway, whether that lode necessarily has mineralization of a commercial grade. Another unknown factor is whether the gap between the fissure mineralization and the lode mineralization may be short enough so that a reasonable expenditure will succeed in bridging it.

CALUMET AND HECLA CONSOLIDATED COPPER CO.,
CALUMET, MICHIGAN.

HYDROTHERMAL EXPERIMENTS WITH COPPER COMPOUNDS.

CHARLES F. PARK, JR.

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INTRODUCTION.

IN view of the interesting results recently obtained on the hydrothermal oxidation and leaching of iron ores [1] it was decided to try similar methods on copper minerals. More than 200 experiments have been completed and the work includes tests on chalcopyrite, chalcocite, covellite, cuprite, malachite, and several artificial salts of copper.

No work known to the writer records in detail the effects of thermal waters on earlier sulphide deposits. It is generally conceded that many sulphides are deposited from hot solutions. When the sulphide deposition stops, do the waters also stop, or, if they continue to flow, what would be their effects on the sulphides? It seems reasonable to suppose that in many natural occurrences, hot waters have passed through pre-existing sul-

[1] Gruner, J. W.: Hydrothermal Oxidation and Leaching Experiments. ECON. GEOL., vol. 25, pp. 697–719, 1930.

phide bodies. One part of the present paper deals with this problem. Another part deals with the reactions of artificial copper compounds, chiefly the chlorides, in steam. This last part is of interest in that it may help to throw light on the origin of such ores as those of Lake Superior, Coro Coro, Bolivia, and other areas where lava flows contain hydrothermally deposited native copper. Some possible applications of the results obtained in the experiments are also discussed.

Little information is available regarding the behavior of copper compounds in water vapor below a temperature of 500° C.[2] Considerably more work has been done with the copper compounds at red heat and above.[3]

This problem was proposed by Dr. J. W. Gruner, and throughout the work he has offered many valuable and helpful suggestions. Dr. R. B. Ellestad, Chemist of the Rockefeller Foundation National Laboratory for Rock Analysis, University of Minnesota, has also contributed valuable advice and suggestions. The various members of the geological faculty at the University of Minnesota have throughout evidenced interest in the work, and various suggestions of theirs have been followed.

APPARATUS AND METHODS USED.

Experiments have recently been made at the University of Minnesota in two types of apparatus. One group was in bombs similar to those described by Gruner;[4] another group was in tube furnaces.

An important feature of one of the bombs is a valve that allows gases to escape slowly through a capillary tubing. This permits the reactions to be completed in one direction. The pressure obtained was close to the steam pressure at the temperature of the particular experiment, plus the partial pressure of any other gas present. A few cubic centimeters of solution were left in the

[2] Foreman, Fred: Hydrothermal Experiments on Solubility, Hydrolysis, and Oxidation of Iron and Copper Sulphides. ECON. GEOL., vol. 24, pp. 811–837, 1929. Regnault, Annales de Chim. et de Phys., vol. 62, p. 378, 1836.

[3] Gautier, M. Armond: Compt. Rend., vol. 142, p. 1465, 1906. Regnault: *op. cit.*

[4] Gruner, J. W.: *op. cit.*, p. 708.

bombs at the end of each experiment. Other bombs used were of closed types.

The second group of experiments was made in an electric tube furnace lined with pyrex glass, through which steam and various gases were passed[5] (Fig. 1). The specimens were placed in

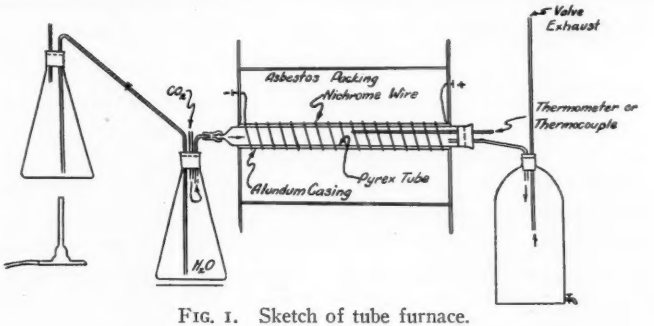

FIG. 1. Sketch of tube furnace.

porcelain boats in the pyrex tubing. Temperatures below 250° C. were recorded by an ordinary mercury thermometer. A Hoskins chromel-alumel thermocouple was used to measure the higher temperatures. Care was taken to exclude all air from the apparatus. All water used was first boiled for at least three minutes. CO_2 from a cylinder was used in some of the experiments. This gas contained 0.1 per cent. impurity, which was not analyzed but was known to contain some oxygen, as shown by tests with yellow phosphorus. Experiments in which this oxygen was or was not removed show essentially the same results and the amount of oxygen present is not considered sufficient to affect the final results of the experiments to an important degree. CO_2 snow was used in a few experiments.

Many of the mineral specimens were polished and examined in reflected light before using. After extraction from the furnace, all materials were studied under the binocular microscope. Some of the minerals were repolished and again examined in reflected light.

[5] Gruner, J. W.: *op. cit.*, p. 707.

Mineral identification was made in reflected light and also by microchemical tests. Difficulty was experienced with finely divided copper, this substance resembling some of the reddish yellow oxides. There is a slight color distinction, and rarely a wire large enough to show ductility was present. Iodine and mercuric chloride tests were especially valuable in the determination of native copper.

EXPERIMENTS.

Two groups of experiments were conducted in the present work. The first group deals with the action of steam, CO_2, H_2S, and HCl vapor, on various sulphides and other copper compounds. The second group was made in order to study the formation of metallic copper in the presence of the chloride radical, Fe_2O_3, and $CaCO_3$. A few experiments were completed to test the solubility of copper in carbonate solutions under high pressures of CO_2 gas (Table VI.).

The materials tested were, for the most part, allowed to cool rapidly (less than two hours); several cooled for about 24 hours. The rate of cooling, up to about a day, does not seem to have any appreciable effect on the end product formed.

The longest time that any of the experiments were continued is one month; many were stopped after one week. It is probable that in a number of the experiments the two oxides and metallic copper did not reach a state of stable equilibrium. The end products are also found to vary somewhat with the quantities of steam and gases used. In all except a few experiments in steam, about four liters of water were used every 24 hours.

The end products that form from all the copper compounds used, when placed in a dynamic system [6] with steam alone, are copper, Cu_2O, and CuO. The temperatures of the experiments range from 110° C. to 530° C. (Table I.)

Materials similar to those that were tried in steam were then placed in the same system with steam and CO_2. Essentially the same results were obtained with or without CO_2 although in a few

[6] A dynamic system is a system in which one or more of the components are in motion.

instances the CO_2 seemed to accelerate the reactions slightly (Table II.).

A number of experiments were conducted with HCl vapor and steam (1% HCl solution). This HCl solution was allowed to drip slowly on a hot disc and the resulting vapor passed through the furnace.[7] The reactions are similar to those in the above experiments but progress is more rapid with materials that contain iron (chalcopyrite, bornite) (Table III.).

In the presence of steam and an excess of H_2S, malachite, cuprite, CuCl, $CuCl_2$, and $CuSO_4$ form chalcocite or covellite up to a temperature of about 500° C. These sulphides are stable so long as the H_2S is in excess of the amounts required to maintain the equilibrium between the solid and the gas. The quantity of the gas required depends upon the temperature and the pressure of the particular experiment. When the H_2S is below the amount required to form such sulphides, the oxides and native copper will form (Table IV.). When the H_2S is greatly in excess of the amount to form Cu_2S (temperature 250° C.) the Cu_2S will have a blue color from the presence of CuS. In some tests chalcocite formed above 500° C. The concentration of the H_2S was about the same as in other experiments in which the chalcocite decomposed.

About 25 experiments were completed using a bomb with a valve (Table V.). Due to the small capacity of the bomb (51 cc.) the reactions could not be continued for a longer time interval than 24 hours. In all the bomb experiments, 25 cc. of boiled water were used. The remainder of the available space in the bomb was filled with a gas, either CO_2 or H_2S. Metallic copper, CuO, Cu_2O, and copper sulphides were all obtained under certain conditions that are stated later.

Some experiments were made in a closed steel bomb lined with copper, gold, or pyrex glass tubing (Table VI.). The individual experiments will be discussed later.

[7] The apparatus for using definite HCl concentrations will be described by J. W. Gruner in a future publication.

RESULTS OF EXPERIMENTS.

Experiments with Chalcopyrite.

Steam.—A specimen of chalcopyrite subjected to a current of steam at temperatures between 200° C. and 300° C. is not stable. Bornite, chalcocite, and magnetite are formed (Figs. 2 and 3). Above about 300° C. the decomposition goes further and CuO, Cu_2O, and copper are formed.

(1) $12CuFeS_2 + 24H_2O \rightarrow 24H_2S + 4Fe_3O_4 + 5CuO + 3Cu_2O + Cu.$

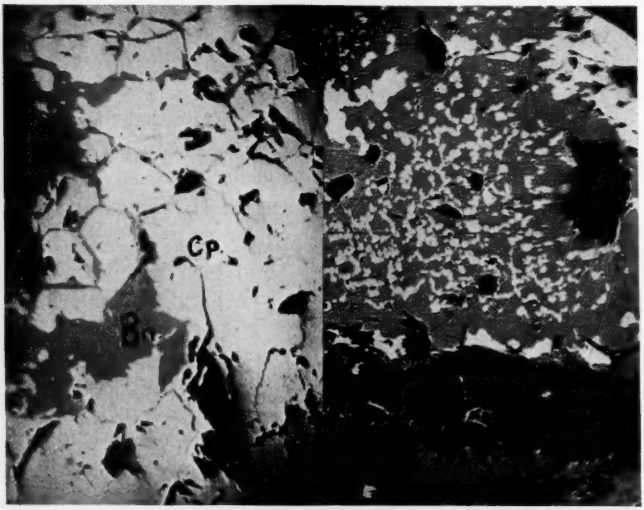

FIG. 2 (left). Polished surface showing bornite developed from chalcopyrite by passing steam over it for 4 days. Temperature 350 C. The bornite is developing around grains of chalcopyrite and along fractures. × 100.

FIG. 3 (right). Photomicrograph showing chalcopyrite (white) subjected to steam for a week at a temperature of 350 C. and changed almost completely to bornite (gray). During the process magnetite was developed in the cracks and vugs (black). × 100.

The reactions written for chalcopyrite will take place providing the H_2S is removed as it is evolved.

TABLE I.

STEAM, DYNAMIC SYSTEM.

Exp. No.	Material	Temp. ° C.	Length of Time —Hrs.	Results
P-3.....	Artificial $CuFeS_2$	200	25	CuO tarnish
P-4a.....	$CuFeS_2$ + pyrrhotite	200	25	Tarnish
P-4b.....	$CuFeS_2$ + Cu_2S	200	25	Tarnish, Cu_5FeS_4, CuS?
P-15c....	$CuFeS_2$ + Cu_2S + FeS_2	265–450	540	Cu_2O, CuO, Fe_2O_3, Fe_3O_4, Cu_5FeS_4, Cu_2S
P-47a....	$CuFeS_2$	280	165	Cu_5FeS_4, intergrowth with $CuFeS_2$, Cu_2S, Fe_3O_4
P-49a....	$CuFeS_2$	280	160	Cu_5FeS_4, intergrowth with $CuFeS_2$, Cu_2S, Fe_3O_4
P-25a....	$CuFeS_2$	340	160	Cu_5FeS_4, intergrowth with $CuFeS_2$, Cu_2S, Fe_3O_4
P-15d....	$CuFeS_2$ + pyrrhotite	350–450	230	CuO, Cu_2O, Fe_2O_3, Fe_3O_4, Cu_5FeS_4, Cu_2S
P-21a....	$CuFeS_2$	450	170	CuO, Cu_2O, Fe_2O_3, Fe_3O_4, Cu
P-30a....	$CuFeS_2$ + calcite	450	170	Cu_5FeS_4, intergrowth with $CuFeS_2$, Cu_2O, Cu_2S, Fe_3O_4, Fe_2O_3
P-53a....	$CuFeS_2$	460	330	Cu_2O, Cu. Fe_2O_3, minor CuO and Fe_3O_4
P-53b....	$CuFeS_2$ + pyrrhotite	460	330	Cu_2O, CuO, Fe_2O_3, Fe_3O_4
P-40b....	Cu_2S + FeS_2	110	160	Unaltered
P-44c....	Cu_2S + FeS_2	160	160	Slight tarnish
P-6a.....	Cu_2S	200	75	Tarnish
P-6b.....	Cu_2S	200	100	Tarnish
P-6c.....	Cu_2S	200	140	Tarnish
P-5.....	Cu_2S + FeS_2 + Cu_5FeS_4	200	25	Tarnish, Cu_5FeS_4 + Fe_3O_4 (both from FeS_2)
P-37a....	Cu_2S + FeS_2	215	170	Tarnish, $CuFeS_2$
P-15a....	Cu_2S + FeS_2	265–450	540	Cu_2O, CuO, Fe_3O_4, Fe_2O_3
P-7a.....	Cu_2S	275	50	Tarnish
P-7b.....	Cu_2S	275	95	Tarnish
P-7c.....	Cu_2S	275	145	Tarnish
P-1.....	Artificial Cu_2S	275–360	45	Cu_2O, Cu. CuO
P-34b....	Cu_2S + FeS_2	280	160	Tarnish, $CuFeS_2$, Cu_5FeS_4
P-1a.....	Cu_2S	305	25	Tarnish
P-25b....	Cu_2S + FeS_2	340	160	$CuFeS_2$, Cu_5FeS_4, Fe_3O_4
P-2a.....	Cu_2S	350	50	Tarnish
P-2b.....	Cu_2S, FeS_2	350	50	$CuFeS_2$, Cu_5FeS_4, Fe_3O_4
P-8a.....	Cu_2S	360	50	Tarnish, CuO, Cu_2O
P-8b.....	Cu_2S	360	117	Cu_2O, CuO
P-8c.....	Cu_2S	360	205	Cu_2O, CuO, Cu
P-52b....	Cu_2S	370	330	Cu_2O, tarnish
P-21b....	Cu_2S, FeS_2	450	170	Cu_2O, Cu, Fe_3O_4, Fe_2O_3
P-30b....	Cu_2S, FeS_2, $CaCO_3$	450	170	Cu_2O, Cu, Fe_3O_4, Fe_2O_3, calcite unchanged
P-53c....	Cu_2S, FeS_2	460	330	Cu_2O, Cu, Fe_3O_4, Fe_2O_3, CuO?
P-40a....	CuS, Cu_2S, $CuFeS_2$	110	155	Cu_2S, $CuFeS_2$, S
P-41a....	CuS, Cu_2S, $CuFeS_2$, FeS_2	450	155	Cu_2O, Cu, CuO, Fe_2O_3, Fe_3O_4

TABLE I.—Continued.

Exp. No.	Material	Temp. ° C.	Length of Time —Hrs.	Results
P-40c....	$CuCl$, Fe_2O_3	110	155	Cu_2O, Fe_3O_4
P-37b....	$CuCl$, Fe_2O_3, $CaCO_3$	215	170	Cu_2O, Cu
P-26b....	$CuCl$	450	140	CuO, Cu_2O?
P-26a....	$CuCl$, $CaCO_3$	450	140	CuO, Cu_2O, Cu
P-23.....	$CuCl$, Fe_2O_3	450	190	CuO, Cu_2O, Cu?
P-38a....	$CuCl$, Fe_2O_3	450	170	CuO, Cu_2O, Cu?, Fe_3O_4
P-41c....	$CuCl$, Fe_2O_3	450	160	CuO, Cu_2O, Cu?, Fe_3O_4
P-38b....	$CuCl$, Fe_2O_3, $CaCO_3$	450	170	CuO, Cu_2O, Cu, Fe_3O_4
P-44a....	$CuCl_2$	160	160	CuO
P-37c....	$CuCl_2$	215	170	CuO
P-45a....	$CuCl_2$, $CaCO_3$ powder, Fe_2O_3	275	175	CuO, $CaCO_3$, greenish
P-45b....	$CuCl_2$, Fe_2O_3	275	175	CuO, Cu?
P-45c....	$CuCl_2$, $CaCO_3$ powder	275	175	CuO
P-47b....	$CuCl_2$, $CaCO_3$, Fe_2O_3	280	165	CuO, Cu, yellowish brown salt
P-47c....	$CuCl_2$, $CaCO_3$, FeS_2	280	165	CuO, Cu, Cu_2O, Cu_2FeS_4, $CuFeS_2$, tarnish
P-47d....	$CuCl_2$	280	165	Cu_2O
P-49b....	$CuCl_2$, Na_2CO_3, $CaCO_3$, Fe_2O_3	280	160	Cu?
P-54b....	$CuCl_2$, on thin layer of Fe_2O_3	370	165	Fe_2O_3, bleached—CuO
P-52a....	$CuCl_2$, $CaCO_3$, Fe_2O_3	370	330	Cu_2O, Cu, CuO, yellowish salt
P-28.....	$CuCl_2$, $CaCO_3$	450	110	Cu_2O, Cu, CuO, yellowish salt
P-38c....	$CuCl_2$	450	170	CuO
P-57a....	$CuCl_2$, on thin layer of Fe_2O_3	450	165	Some migration of the Fe_2O_3, not conclusive
P-57b....	$CaCl_2$, on thin layer of Fe_2O_3	450	165	Some migration of the Fe_2O_3, not conclusive
P-51b....	$CuCl_2$, $CaCO_3$	460	240	Cu, brownish salt
P-51c....	$CuCl_2$, Cu_2O	460	240	Cu, recrystallized Cu_2O, yellowish salt
P-51a....	$CuCl_2$, Fe_2O_3	460	240	Cu, Cu_2O
P-34a....	Cu_2O	280	160	Stable
P-19a....	Cu_2O	450	110	Stable
P-35a....	Cu_2O	450	165	Stable, CuO?
P-19c....	Cu_2O, chalcotrichite	450	110	CuO
P-19b....	CuO	450	110	CuO
P-43a....	Cu_2O	525	160	Stable—Some yellowish salt
P-44b....	$CuCO_3 . Cu(OH)_2$, malachite	160	160	Thin layer of CuO
P-43b....	$CuCO_3 . Cu(OH)_2$, malachite	525	160	CuO
P-34c....	$CuSO_4 + FeS_2$	280	160	Tarnish
P-35b....	$CuSO_4$, $CaCO_3$, Fe_2O_3	450	160	Cu_2O, CuO, Cu
P-35c....	$CuSO_4$, $CaCO_3$, FeS_2	450	160	Tarnish
P-41b....	$CuSO_4$, $CaCO_3$, Fe_2O_3	450	160	Cu_2O, Cu?, very minor CuO
P-43c....	$CuSO_4$	525	160	CuO, yellowish salt

When the temperature is above about 258° C. magnetite is not stable in steam alone, and hematite forms[8] (Dynamic system). The reaction may then be written.

(2) $$2Fe_3O_4 + H_2O \rightarrow 3Fe_2O_3 + H_2.$$

In some of the reactions cited later, it is difficult to account for the reduction of part of the copper unless hydrogen is taken into consideration. It is thought that the hydrogen, freed by the breaking up of H_2O at the time of oxidation of magnetite to hematite may act further on the CuO and Cu_2O and tend to form more copper. If ferrous silicates are present they may also be oxidized and give off hydrogen.[9] According to Longmuir,[10] who studied alloys at high temperatures, iron may be a deoxidizer of copper. It is thought from a study of some of the following reactions that ferrous oxide has a somewhat similar deoxidizing effect. It is known that the rate of oxidation of ferrous iron is greatly increased by copper in solution.[11]

With chalcopyrite in steam at atmospheric pressure, reaction starts at about 200° C. (Table I.), but proceeds slowly. At 400° C. the action is sufficiently rapid so that at the end of a week a small polished specimen is almost completely altered. Bornite and magnetite form first; the bornite then changes to chalcocite and magnetite with small amounts of covellite. Further reactions give CuO, Cu_2O, copper, and hematite. The equations may be summed up as follows:

(3) $$7CuFeS_2 + 9H_2O \rightarrow Cu_5FeS_4 + 9H_2S + 2Fe_3O_4 + Cu_2S + O,$$
$$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3,$$
$$3Cu_5FeS_4 + 4H_2O \rightarrow 7Cu_2S + CuS + Fe_3O_4 + 4H_2S,$$
$$3Cu_2S + 2Fe_3O_4 + 3H_2O \rightarrow 2Cu_2O + 2Cu + 3Fe_2O_3 + 3H_2S.$$

In these equations part of the Cu_2S probably oxidizes directly, as explained under the heading of chalcocite.

[8] Gruner, J. W.: *op. cit.*, p. 708.

[9] Gautier, M. Armond: Compt. Rend., vol. 132, pp. 189–194, 1901.

[10] Longmuir, P.: Deoxidation of Copper and Its Alloys. Foundry, vol. 40, p. 460, 1913.

[11] Locke, Augustus: Leached Outcrops as Guides to Copper Ore, pp. 37; 40–41, 1926.

CuS is found as a thin coating on the surface and along cracks. This substance, corresponding to covellite, is not very stable under the conditions used. It changes rapidly to CuO.

$$CuS + H_2O \rightarrow CuO + H_2S. \quad (4)$$

As stated by Tolman and Clark,[12] covellite is not stable at room temperatures in the presence of water, but forms chalcocite and sulphur. The reaction, in steam, possibly takes place according to the following steps:

$$2CuS + H_2O \rightarrow Cu_2S + S + H_2O, \quad (5)$$
$$Cu_2S + S + 2H_2O \rightarrow 2CuO + 2H_2S.$$

The presence of CuO, Cu_2O, and Cu, seen as end products in equations (1) and (3), may be explained by auto-oxidation or the oxidation of one molecule at the expense of another of the same kind. According to Treadwell and Hall,[13] this type of reaction is of common occurrence. There are several well known examples. When a manganese salt is heated in sodium carbonate (ordinary bead test) Na_2MnO_4 is obtained. If the bead is then dissolved in a hydrochloric acid solution, part of the manganese is oxidized to the permanganic state ($NaMnO_4$) and part of it is reduced, forming MnO_2. From the results obtained in a number of experiments it is thought that this process of simultaneous oxidation and reduction commonly takes place with copper compounds. It is realized that the length of time the experiments were continued is important and that, given sufficient time, one stable end product might be the final result. It is felt, however, that many of the reactions reached practically a condition of equilibrium.

Several experiments with chalcopyrite resulted in a subgraphic intergrowth between bornite and chalcopyrite (Fig. 3). This intergrowth is thought to have been formed during the removal of part of the iron in the chalcopyrite. The iron yielded small crystals of magnetite in holes and along cracks developed in the specimen, implying a migration of the iron. The intergrowth

[12] Tolman, C. F., Jr., and Clark, J. D.: Copper in Electrolytic Solutions, ECON. GEOL., vol. 9, pp. 575–576, 1914.

[13] Treadwell and Hall: Analytical Chemistry (Qualitative Analysis), p. 179, 1930.

TABLE II.

STEAM + CO_2, DYNAMIC SYSTEM.

Exp. No.	Material	Temp. ° C.	Length of Time —Hrs.	Results
P-10a....	$CuFeS_2$, fused with Na_2CO_3	195	72	Cu_2S, Fe_3O_4
P-9a.....	$CuFeS_2$	200–350	140	Cu_5FeS_4, intergrowth with $CuFeS_2$, Cu_2S, Cu_2O, Fe_3O_4, Fe_2O_3
P-12a....	$CuFeS_2$, fused with Na_2CO_3	200–360	235	Tarnish
P-9b.....	$CuFeS_2$, powdered	200–360	115	Cu_2O, Fe_3O_4
P-20b....	$CuFeS_2$	340	310	Superficial, Cu_5FeS_4, Fe_3O_4
P-31a....	$CuFeS_2$, $CaCO_3$	340	170	Cu_5FeS_4, intergrowth with $CuFeS_2$, Fe_3O_4, Cu_2S
P-20c....	$CuFeS_2$, Fe_7S_8	340	310	Superficial, Cu_5FeS_4, Fe_3O_4
P-9d.....	$CuFeS_2$	350	50	Cu_2O, Fe_2O_3, Fe_3O_4
P-14b....	$CuFeS_2$	400	65	Cu_2O, Fe_2O_3, Fe_3O_4
P-10b....	Cu_2S	195	70	Unaltered
P-12b....	Cu_2S, fused with Na_2CO_3	200–360	140	Cu_2O, Cu
P-20a....	Cu_2S	340	310	CuO?, superficial
P-31b....	Cu_2S, FeS_2, $CaCO_3$	340	170	Cu_5FeS_4, $CuFeS_2$, Fe_3O_4
P-14a....	Cu_2S	400	65	Tarnish, Cu_2O
P-22.....	CuCl, $CaCO_3$	340	135	Cu_2O, Cu, CuO(?)
P-9c.....	CuCl	350	45	Cu_2O
P-29.....	$CuCl_2$, $CaCO_3$	340	110	Cu_2O, CuO, Cu
P-32a....	$CuCl_2$, $CaCO_3$, Fe_2O_3	340	170	Cu_2O, CuO, Cu, $CaCl_2$
P-31c....	$CuCl_2$, $Fe_2O_3 . 3H_2O$, $CaCO_3$	340	170	Cu, yellow salt on calcite
P-14e....	Cu_2O	400	65	Stable
P-14d....	Cu_2O (Chalcotrichite)	400	65	CuO
P-9g.....	CuO	120–200	40	CuO
P-12c....	CuO	200–360	270	CuO
P-9f.....	CuO	250	20	CuO
P-9e.....	$CuCO_3$	250	20	CuO
P-9h.....	$CuCO_3 . Cu(OH)_2$ (Malachite)	120–200	40	Some CuO
P-32h....	$CuSO_4$, $CaCO_3$, Fe_2O_3	340	170	CuO, yellow salt, $CaSO_4 . 2H_2O$

cannot be considered strictly a replacement phenomenon, as defined by Lindgren,[14] nor is it the same as the intergrowth obtained by Wandke, Schwartz, Aubel,[15] and others, who formed similar textures by unmixing of the constituents.

[14] Lindgren, W.: Mineral Deposits, 3d ed., p. 105, 1928.

[15] Wandke, A.: Molecular Migration and Mineral Transformation, ECON. GEOL., vol. 21, pp. 166–171, 1926. Schwartz, G. M.: Intergrowths of Bornite and Chalcopyrite, ECON. GEOL., vol. 26, pp. 186–201, 1931. Van Aubel, Réne: Sur les minerais de Cuivre, etc., Soc. Franc. Miner., Bull. 51, pp. 161–165, 1928.

No good intergrowths were obtained in the chalcocite formed from a breaking down of chalcopyrite, although several of the specimens have a suggestive orientation of the mineral with bornite. The contacts are mostly gradational from one mineral into the other.

When heated, the specimens are commonly enlarged and shattered, thus facilitating removal of the H_2S and increasing the surface exposed to the steam. If pyrite is present in the specimen, it especially expands and shatters the enclosing material. Pyrite begins to decompose[16] in bomb experiments at a temperature of about 165° C.

Steam and CO_2.—When chalcopyrite is subjected to steam and CO_2 at atmospheric pressure and temperatures above 200° C. the same reactions occur as with steam alone (Table II.).

Steam and H_2S.—In a current of steam and H_2S, chalcopyrite decomposes at temperatures above 200° C. (Table IV.). The chalcopyrite forms a series grading into bornite and chalcocite. The contacts are not sharp but fade gradually into each other. This is especially true of the chalcocite-bornite contacts. Treatment for a week produces no notable change beyond the chalcocite stage. Chalcocite forms at temperatures as high as 530° C. but in a few specimens at this high temperature CuO, Cu_2O, and Cu also form. In one specimen (P–46a) metallic copper and chalcocite are developed together but no oxides can be detected. The iron forms magnetite (hematite at the higher temperatures). The intergrowth between chalcopyrite and bornite is well developed, as in steam alone. Some iridescent bluish stain forms on the surface of the chalcopyrite but in amounts too small to be determined.

Experiments with Chalcocite and Covellite.

Steam.—When chalcocite is heated alone in steam, Cu_2O is the end product obtained between the temperatures of about 250° C. and 350° C. (Table I.). According to Foreman,[17] the reaction between steam and chalcocite starts at between 210° and 250° C.

[16] Foreman, *op. cit.*, p. 830.

[17] Foreman, *op. cit.*, p. 832.

Some tarnish forms on a polished surface of chalcocite at temperatures as low as 200° C. The reaction proceeds slowly at this temperature and at the end of a month only a very thin coating is to be found on the polished surface. The reaction is accelerated somewhat at a temperature of about 250° C. but it is only at a temperature of 300° C. that the action becomes appreciable within a week. The reaction below 350° C. may be expressed by equation 6.[18]

(6) $$Cu_2S + H_2O \rightarrow Cu_2O + H_2S.$$

In many of the experiments a small amount of CuO has been observed.

With chalcocite in steam above 350° C. metallic copper in small wires and crystals is formed. The reaction given above no longer answers the conditions. The equation may be:—

(7) $$2Cu_2S + 2H_2O \rightarrow Cu_2O + CuO + Cu + 2H_2S.$$

Since quantitative analyses of the resulting constituents were not made, the above equation is qualitative only. There are several other possible equations that will furnish the same end products in different proportions. One suggested by Foreman's work [19] would furnish SO_2 and sulphur as end products.

(8) $$8Cu_2S + 6H_2O \rightarrow 10Cu + 2CuO + 2Cu_2O + 6H_2S + SO_2 + S.$$

The second equation is more probable than the first because the relative amounts of Cu, CuO, and Cu_2O more nearly fit the observed end products, but no SO_2 has been detected. It is possible that the quantities were so small as to escape detection. In a number of experiments a very small amount of free sulphur was formed (dissolved in CS_2).

When pyrite is present in chalcocite the alteration of the chalcocite is much more rapid than when pyrite is absent. The breaking down of pyrite, since it involves a swelling effect, may accelerate mechanically the disintegration of the chalcocite. It is thought that the additional surface exposed by this swelling and

[18] Foreman, *op. cit.*, p. 833.
[19] Foreman, *op. cit.*, p. 832.

TABLE III.

STEAM + HCl, DYNAMIC SYSTEM.

Exp. No.	Material	Temp. ° C.	Length of Time —Hrs.	Results
P-11.....	$CuFeS_2$	240	76	Tarnish—Fe_3O_4, Cu_5FeS_4
P-24a....	$CuFeS_2$	240	75	Fe_3O_4, Cu_5FeS_4, Cu_2S, superficial
P-27a....	$CuFeS_2$, Fe_7S_8	270	40	Fe_3O_4, Cu_5FeS_4, Cu_2S, superficial
P-36a....	$CuFeS_2$	275	75	Fe_2O_3, Fe_3O_4, Cu_5FeS_4, Cu_2S, Cu_2O(?)
P-24b....	Cu_2S, FeS_2	240	75	CuO, Fe_3O_4, Cu_5FeS_4, $CuFeS_2$
P-27b....	Cu_2S, FeS_2	270	40	CuO, Fe_3O_4
P-36b....	Cu_2S	275	75	Tarnish

TABLE IV.

STEAM + H_2S, DYNAMIC SYSTEM.

Exp. No.	Material	Temp. ° C.	Length of Time —Hrs.	Results
P-55b....	$CuFeS_2$	250	165	Cu_5FeS_4, Fe_3O_4, Cu_2S
P-33a....	$CuFeS_2$	450	160	Cu_5FeS_4, intergrowth with $CuFeS_2$, Fe_3O_4, Cu_2S
P-48a....	$CuFeS_2$	460	165	Cu_5FeS_4, intergrowth with $CuFeS_2$, Fe_3O_4, Cu_2S
P-48b....	$CuFeS_2$, pyrrhotite	460	165	Cu_5FeS_4, intergrowth with $CuFeS_2$, Fe_3O_4, Cu_2S
P-46a....	$CuFeS_2$	525	160	Fe_2O_3, Fe_3O_4, Cu_2S, Cu.
P-46b....	Cu_2S	525	160	Glossy coating, Cu on one end
P-48c....	CuS, Cu_2S, FeS_2	460	165	Cu_2S, Fe_2O_3, Fe_3O_4, Cu_5FeS_4 intergrowth with $CuFeS_2$
P-17b....	CuCl	450	50	Cu_2S
P-17a....	CuCl, $FeCl_3$	450	50	Cu_2S
P-16.....	CuCl	530	25	Cu_2S, Cu_2O, Cu?
P-55a....	$CuCl_2$	250	165	Cu_2S, CuS
P-56a....	$CuCl_2$	360	165	Cu_2S (84%), CuS (16%)
P-46c....	$CuCl_2$	525	160	Cu_2S
P-18.....	Cu_2O	450	65	Cu_2S
P-56b....	$CuCO_3.Cu(OH)_2$, malachite	360	165	Cu_2S
P-33b....	$CuCO_3.Cu(OH)_2$, malachite	450	160	Cu_2S, brownish salt

subsequent shattering is an important factor in the breakdown of chalcocite. It is also possible that the iron has a deoxidizing effect as suggested previously.

Covellite, as stated above, is not stable in steam. It forms chalcocite at and above the lowest temperatures used (110° C.) (Table I.) Free sulphur collects in small yellowish-white spots on the surface. After forming chalcocite, the material behaves in the same manner as the chalcocite reactions already described.

A number of specimens of chalcocite originally containing pyrite, after being in steam, show the pyrite completely altered to chalcopyrite. Around this chalcopyrite is a zone of bornite and this in turn fades gradually into unchanged chalcocite. The lowest temperature at which the formation of chalcopyrite from pyrite takes place is about 180° C. At 160° C., after a week, no chalcopyrite is found. At a temperature of 215° C. (in a week) the pyrite is not entirely altered and when the specimen is repolished, small shattered and corroded fragments of pyrite are seen to be surrounded by chalcopyrite.[20] When the alteration is allowed to proceed beyond the formation of chalcopyrite the changes take place as described under chalcopyrite and chalcocite. The associations and textures developed might easily be mistaken for the result of supergene alteration, in a study of polished sections.

When chalcocite and magnetite are present in steam the reaction that takes place may be written:—

(9) $3Cu_2S + 2Fe_3O_4 + 3H_2O \rightarrow 2Cu_2O + 2Cu + 3Fe_2O_3 + 3H_2S.$

This reaction is explained further under the heading of chalcopyrite.

Steam and CO_2.—The results, in a dynamic system, with chalcocite in CO_2 and steam, are practically the same as the results in steam alone (Table II.).

Steam and H_2S.—As mentioned previously some specimens of chalcocite are stable in steam and H_2S at temperatures above 500° C. (Table IV.). There are, in every case, small clusters of re-

[20] Wandke, A., *op. cit.* Chalcopyrite and bornite were formed in dry heat by a diffusion of chalcocite and pyrite.

crystallized Cu_2S on the surface of the specimen. In some specimens CuO, Cu_2O, and small wires of metallic copper are formed. This again may be an example of simultaneous oxidation and reduction.

Experiments with Cuprous Chloride (CuCl).

Steam.—When CuCl is put in steam alone (dynamic system) CuO is the stable end product formed (temperature between 110°–450° C.) (Table I.). When a piece of calcite is introduced into the CuCl, the calcite is covered with a layer of Cu_2O crystals and needles. Some metallic copper is present at the end of a week, especially on the side of the calcite not exposed directly to the steam. This copper is in two forms, small wires and crystals. Some of the wires are large enough to bend and thus serve as a check on the chemical reactions used to identify the copper.

When natural hematite (massive hematite from the Penokee-Gogebic District) is mixed with CuCl, in steam, at temperatures varying from 110° C. to 450° C. Cu_2O forms in very excellent crystals. Small amounts of CuO and a few small wires resembling copper are present but copper has not been definitely identified. Part of the hematite is reduced to magnetite.

Natural hematite and calcite in a current of steam with CuCl give results similar to those obtained when CuCl and calcite were used. Considerable metallic copper and Cu_2O are formed. In addition to this the hematite is partially reduced to magnetite. This reaction takes place at 450° C., the highest temperature used with the materials.

Steam and CO_2.—In the presence of CO_2 and steam the experimental results are the same as those obtained using steam alone (Table II.).

Steam and H_2S.—Cu_2S forms from CuCl in steam with an excess of H_2S, at temperatures near 450° C. (Table IV.).

Bomb with valve.—A number of experiments were conducted on combinations of CuCl, Fe_2O_3, $CaCO_3$, H_2S, and CO_2, using a bomb with a valve (Table V.). The temperatures used were between 175° and 300° C.

With CuCl (CO_2 atmosphere) and 25 cc. of water in the bomb, nothing takes place. When calcite is introduced, Cu_2O forms a layer covering the calcite. If the atmosphere is changed from CO_2 to H_2S, and the solution saturated with H_2S, copper sulphides result. Cu_2O is also formed on the calcite with some spots that may be metallic copper.

When hematite and CuCl are placed in an atmosphere of H_2S, most of the residue left in the bomb is made up of copper sulphides but some Cu_2O and possibly metallic copper are formed; ferrous sulphide, FeS, may also be present.

CuCl, hematite, and calcite were placed in the bomb in an atmosphere of CO_2 (temperature 175°–300° C.). Some Cu_2O results after about 24 hours but the majority of the material present is CuO. When the atmosphere is H_2S, instead of CO_2, Cu_2O, CuO, copper sulphides and copper are produced. The hematite is partially reduced to magnetite and there is no ferrous iron in solution. The calcite crystals are rounded and corroded; some $CaCl_2$ also is present. An excess of H_2S or an excess of HCl prevents the reaction from going in only one direction. This conclusion is reached from a study of the reaction involved and is further substantiated by experiments.

Experiments in a bomb with a valve (temperature 175° C. and CO_2) using 0.5 grams CuCl, a chip of hematite, a chip of calcite, and 25 cc. of boiled water resulted in the calcite being covered with a green basic chloride, answering some of the physical properties of atacamite ($Cu_2ClH_3O_3$). The same materials were then used at a temperature of 225° C. and none of the basic chloride was obtained.

Experiments with Cupric Chloride ($CuCl_2$).

Steam.—When $CuCl_2$ alone is put in steam, CuO is formed at temperatures between 110° and 530° C. (Table I.). There appears to be a simple reaction. HCl is found in the discharged steam.

(10) $$CuCl_2 + H_2O \rightarrow 2HCl + CuO.$$

The end products in all of the experiments are found to vary

somewhat with the amount of steam passed through the furnace. This is especially well seen in the experiments with $CuCl_2$. Small tubes containing some $CuCl_2$ and packed tightly with calcite or glass wool were placed in the furnace. Only a very small amount of steam could pass through the tubes. At the end of a week the

TABLE V.

BOMB WITH A VALVE, DYNAMIC SYSTEM.

Exp. No.	Material	Temp. ° C.	Length of Time —Hrs.	Results
Q-5.....	25 cc. H_2O, .5 g. CuCl, Fe_2O_3, $CaCO_3$, H_2S	175	35	Cu_2S, Cu_2O, atacamite, SO_4
Q-6.....	25 cc. H_2O, .5 g. CuCl, $CaCO_3$, H_2S	175	20	Cu_2S, Cu_2O, Cu, SO_4
Q-9.....	25 cc. H_2O, .5 g. CuCl, Fe_2O_3, H_2S	175	20	Cu_2S, Cu_2O, Cu, Fe^{++}
Q-10.....	25 cc. H_2O, .5 g. CuCl, Fe_2O_3, $CaCO_3$, CO_2	175	35	Cu_2S, Cu_2O, Cu, Fe_3O_4
Q-14.....	25 cc. H_2O, .1 g. CuCl, Fe_2O_3, $CaCO_3$, H_2S	175	12	Cu_2S, Cu_2O, Cu, FeS, SO_4
Q-8.....	25 cc. H_2O, .5 g. CuCl, Fe_2O_3, $CaCO_3$, H_2S	225	20	Cu_2S, Cu_2O, Cu?, CuO
Q-7.....	25 cc. H_2O, .5 g. CuCl, Fe_2O_3, $CaCO_3$, CO_2	225	25	Cu_2O, CuO
Q-3.....	25 cc. H_2O, .5 g. CuCl, Fe_2O_3, H_2S	225	20	Cu_2O, Cu_2S, Cu, Fe^{++}, Fe^{+++}, SO_4
Q-15.....	25 cc. H_2O, .1 g. CuCl, Fe_2O_3, $CaCO_3$, H_2S	225	25	Cu_2O, Cu_2S, Cu, FeS
Q-4.....	25 cc. H_2O, .5 g. CuCl, Fe_2O_3, $CaCO_3$, H_2S	275	25	Cu_2O, Cu_2S, Cu
Q-11.....	25 cc. H_2O, .5 g. CuCl, Fe_2O_3, SiO_2, H_2S	275	25	Cu_2S, Cu?, Fe^{++}, Fe^{+++}, SO_4, Fe_3O_4
Q-12.....	25 cc. H_2O, .5 g. CuCl, Fe_2O_3, SiO_2, H_2S	275	20	Cu_2S, Cu?, Fe^{++}, Fe^{+++}, SO_4, Fe_3O_4
Q-13.....	25 cc. H_2O, .1 g. CuCl, H_2S	275	25	Cu_2S
Q-20.....	25 cc. H_2O, .2 g. $CuCl_2$, Fe_2O_3, $CaCO_3$, CO_2	250	6	Cu_2O, Cu?, CuO, atacamite
Q-19.....	25 cc. H_2O, .2 g. $CuCl_2$, Fe_2O_3, $CaCO_3$, H_2S	300	15	Cu_2S, FeS_2

contents were examined and the copper was found to be present almost entirely as a green basic chloride, insoluble in water. A small amount of an undetermined yellow copper salt was present.

With $CuCl_2$ and a chip of calcite (between temperatures of 210° and 450° C.) in a current of steam, CuO, Cu_2O, and Cu

are formed. The copper is present either as small crystals or in wires that are made up of many tiny crystals. The calcite is covered with a layer of fine black powder (CuO) and a brownish salt of unknown composition, possibly finely divided copper. Here again there are three end products. Since the $CuCl_2$ is already oxidized, auto-oxidation cannot be called upon to explain the results. From attempts to write the equation for the reaction it is seen that there is sufficient oxygen for the formation of CuO from all of the $CuCl_2$. The reaction is not understood unless part of the oxygen passes off as a gas.

The reactions involving the use of $CuCl_2$ and calcite give, in general, the same results as those obtained by using CuCl and calcite. When hematite is added to the $CuCl_2$ and calcite, as much or more copper is formed than with CuCl, hematite, and calcite (Table I.). The individual crystals and wires are very small, the largest seen being about 1 mm. long. These crystals and wires, however, are numerous and occur both on the calcite and on the hematite. The copper on the hematite is confined almost entirely to the edges of the Fe_2O_3 fragments. Considerable quantities of both CuO and Cu_2O are formed and some $CaCl_2$ crystals are deposited on the calcite.

With $CuCl_2$ and hematite in steam, at all temperatures used, CuO, Cu_2O, and Cu are formed.

When a crystal of pyrite is covered with $CuCl_2$ and placed in steam for a week at 280° C., chalcopyrite and bornite are formed as a thin layer coating the pyrite.

Steam and CO_2.—The reactions in steam and CO_2 are similar to those obtained in steam alone (Table II.).

Steam and H_2S.—An analysis of the sulphide formed from $CuCl_2$ (one week at a temperature of 360° C.) in a current of steam and H_2S gave 16.06% CuS and 83.94% Cu_2S.

Bomb With Valve.—Several experiments were completed with $CuCl_2$, Fe_2O_3, and $CaCO_3$, in an atmosphere of H_2S (Table V.). The results are almost the same as those obtained using CuCl under similar conditions. In the presence of finely divided sulphides a small amount of metallic copper is difficult to detect.

The presence of copper was not definitely determined in any of the bomb experiments but some of the residue suggests its presence.

Closed Bomb.—In a closed bomb with $CuCl_2$, hematite, and calcite, in an atmosphere of H_2S (temperature 300° C.), the following equation may be written.

$$(11) \quad 2CuCl_2 + Fe_2O_3 + 5H_2S + 2CaCO_3 \rightarrow Cu_2S + 2FeS_2 + 2CaCl_2 + 5H_2O + 2CO_2.$$

Good crystals of pyrite are formed on the hematite (Table VI.).

Experiments with Cuprous Oxide (Cu_2O).

Steam.—Several specimens of cuprite and of chalcotrichite, Cu_2O (the latter from Bisbee, Arizona), were tried in the dynamic system in steam alone (Table I.). According to experimental work by Palmer, Dunn,[21] and others, Cu_2O begins to oxidize in air to CuO at a temperature of about 165° C. This temperature does not hold in steam alone. At a temperature of 450° C. chalcotrichite is completely changed to CuO, cuprite is scarcely altered. Several specimens of cuprite were subjected to steam, using temperatures up to 450° C. The results in each case show practically no alteration. A slightly darker color may be due to the formation of a very small amount of CuO. The color is still lighter than much natural cuprite.

Steam and CO_2.—The results of the experiments using cuprite and chalcotrichite in steam and CO_2 are similar to those obtained in steam alone (Table II.). The results of one experiment are particularly interesting (P–14d and P–14e). Cuprite and chalcotrichite were used at a temperature of 400° C. and the material was removed from the furnace after a period of 66 hours. The chalcotrichite changed completely to CuO; the cuprite was practically unaltered. From this and similar results obtained in steam alone it is seen that chalcotrichite is less stable under the

[21] Palmer, W. C.: A Study of the Oxidation of Copper and the Reduction of Copper Oxide by a New Method. Proc. Roy. Soc. (London), 103A, pp. 444–461, 1923. Dunn, J. S.: Proc. Roy. Soc. (London), 111A, p. 210, 1926.

TABLE VI

CLOSED BOMB

Exp. No.	Material	Temp. ° C.	Length of Time —Hrs.	Bomb	Results
C-1...	10 cc. H_2O, 1 g. $MgCO_3$, 1 g. Na_2CO_3, Cu foil, 1 g. CO_2 ice	300	75	Pyrex tube in steel bomb	Reacted with glass
C-2...	10 cc. H_2O, .5 g. $MgCO_3$, .5 g. Na_2CO_3, Cu, 1 drop water glass, 1 g. CO_2	300	75		Reacted with glass
C-3...	10 cc. H_2O, .5 g. $MgCO_3$, .5 g. Na_2CO_3, 1 drop water glass, 2 g. CO_2	300	260	Copper tube in steel bomb	Small Cu crystals in SiO_2 gel. (clouds)
C-4...	10 cc. H_2O, .5 g. $MgCO_3$, .5 g. K_2CO_3, 1 drop water glass, 2 g. CO_2	300	260		Small Cu crystals in SiO_2 gel. (clouds)
C-5...	10 cc. H_2O, .5 g. $MgCO_3$, .5 g. Na_2CO_3, Cu wire, 2 drops water glass + 2 g. CO_2	300	210	Gold	Small Cu crystals in SiO_2 gel. (clouds)
C-6...	10 cc. H_2O, .5 g. $MgCO_3$, .5 g. Na_2CO_3, Cu wire, 2 drops water glass CO_2 atm.	300	185		SiO_2 gel. only trace of copper
C-18..	25 cc. H_2O, .2 g. $CuCl_2$, Fe_2O_3, $CaCO_3$, H_2S atm.	300	24		FeS_2, copper sulphides

conditions of the experiments than cuprite. The experiments also show that cuprite, at least for short periods (one week) is stable in steam and CO_2, at temperatures up to 450° C. and at atmospheric pressure.

Steam and H_2S.—Cuprite goes to Cu_2S in the presence of H_2S and steam, at temperatures below 530° C. (Table IV.).

Experiments with Copper Carbonates.

Steam.—Malachite heated alone in steam, between temperatures of 160°–525° C., goes to CuO (Table I.).

Steam and CO_2.—After malachite ($CuCO_3 \cdot Cu(OH)_2$) is exposed to steam and CO_2 for a period of 40 hours, at a temperature ranging from 120° to 200° C., it contains a considerable amount of CuO. This shows that malachite is not stable at atmospheric pressures in steam and CO_2 (Table II.).

$CuCO_3$ salt placed in steam and CO_2 at a temperature of 250° C. for 18 hours changes completely to CuO.

Steam and H_2S.—Chalcocite is formed when malachite is heated in steam and H_2S at a temperature of 450° C. (Table IV.).

Some material resembling malachite in appearance and properties was accidentally formed on the copper lid of a closed steel bomb. This bomb was under a partial pressure of CO_2 of at least 300 pounds. The temperature was 188° C. The green substance was in microscopic botryoidal masses. In several other experiments a green salt resembling malachite was found and it seems that under the proper conditions of pressure it may be possible to form malachite at temperatures slightly above the boiling point of water.

Experiments with Copper Sulphate ($CuSO_4$).

Steam.—$CuSO_4$, when placed in the dynamic system in steam, for a week, at a temperature of 450° C. forms CuO and small quantities of an unknown yellow salt.

At a temperature of 110° C. $CuSO_4$, in a dynamic system with steam, in the presence of calcite and hematite (period of one week) goes almost completely to Cu_2O, yielding some exceptionally fine crystals. A few spots of CuO are also present. When similar materials ($CuSO_4$, hematite, and calcite) are placed in the same system for a week at a temperature of 450° C. most of the $CuSO_4$ turns to CuO and to a pale yellow or buff colored salt (possibly a basic sulphate of copper). Some Cu_2O is present both on the calcite and on the hematite, although this oxide, Cu_2O, is not nearly as abundantly formed as at lower temperatures (Table I.).

Pyrite and $CuSO_4$ were tried in steam at a temperature of 280° C. for a week. At the end of this period the pyrite was changed to bornite and some chalcopyrite (superficially). The pyrite in this experiment was not shattered.

Steam and CO_2.—$CuSO_4$ was heated in steam and CO_2 at a temperature of 340° C. for almost a week (Table II.). The material was mixed with hematite and calcite, the same substances

that furnished copper in the presence of both CuCl and $CuCl_2$. In order to have the conditions exactly the same, $CuSO_4$ and $CuCl_2$, along with calcite and hematite, were placed in a porcelain boat, side by side but not touching. In the case of the chloride, metallic copper is found in considerable amounts whereas none is found with the sulphate. There is some reaction between the sulphate and the calcite, as shown by the presence of some $CaSO_4 \cdot 2H_2O$ (gypsum) crystals and a brownish yellow stain on the calcite. A few crystals of CuO and at least one crystal of Cu_2O are present.

Experiments with Copper and Alkaline Carbonates.

The fact that metallic copper may be transported in alkaline carbonate solutions was discovered by Dr. J. W. Gruner. Some crystals of copper were accidentally obtained while conducting experiments in a bomb containing a copper lid. Several experiments have been performed in order to check this result (Table VI.).

The best results were obtained by using a pure gold closed bomb of 50 cc. capacity; 10 cc. H_2O, 0.5 grams Na_2CO_3, 0.5 grams $MgCO_3$, 2 grams CO_2 snow, 2 drops of sodium silicate (water glass), and a small piece of No. 26 copper wire loosely folded and furnishing considerable surface were added. The experiment was continued for about 10 days at a temperature of 300° C. The cooling time was about 6 hours. The contents of the bomb include a bluish colored gel which in several instances is given a pinkish tint by numerous microscopic crystals of copper. (The crystals are clearly visible when magnified 80 times.) In some instances these crystals are so numerous as to cloud the gel.

One or two drops of sodium silicate were added to each of the experiments. The function of this silicate is to form a gel that will trap and hold the small crystals of copper, thus making them visible. Under ordinary conditions there is some hydrolysis of sodium silicate with the consequent formation of NaOH, which dissolves copper. However, in the presence of CO_2 this hydroxide would immediately form sodium bicarbonate and there

would be no reaction with the copper. No copper has been found in any of the solutions remaining in the bombs.

Between one and two grams of CO_2 snow were added to each of the experiments in which copper has been transported. This gives a maximum partial (CO_2) pressure of about 42 atmospheres or 625 pounds.

When the experiment is performed using only one atmosphere of CO_2 gas (other constituents the same as above, 10 cc. H_2O, 0.5 grams Na_2CO_3, 0.5 grams $MgCO_3$, and two drops of sodium silicate) only a trace of copper is found in the silica gel. This experiment was subjected to the same conditions as those in which copper was transported, 300° C. for about 10 days.

The results are interesting because they show that metallic copper may be transported and recrystallized in an alkaline carbonate solution at high temperatures and pressures. The method of transportation of the copper is entirely speculative; there are several possibilities. It may be carried in solution under the conditions of the experiments or it may be moved in the colloidal state. Upon cooling and decreasing the CO_2 pressure, the copper is redeposited.

APPLICATION OF THE EXPERIMENTAL RESULTS TO DISTRICTS.

No extensive study of the literature has been made in an attempt to find possible applications of the experimental facts disclosed. There are, in general, three classes of reactions. The first is the formation of the oxides, CuO and Cu_2O, and metallic copper, by the action of steam on sulphides. These substances (CuO, Cu_2O, and Cu) were formed from all types of sulphides used, in the absence of air. The second type of reaction brought out in the work is the formation of metallic copper and the oxides directly from the chloride solutions, and the third, the transportation of copper in alkaline carbonate solutions.

The first class of results should be kept in mind wherever hot waters have traversed a deposit of the copper sulphide minerals. Such an application might be found at Santa Rita, New Mexico, where native copper has been found in a drill hole at a depth of

1300–1400 feet.[22] There is in this district considerable evidence of hydrothermal alteration of the country rock such as sericitization and chloritization. It seems reasonable to suppose that in some districts, before the hot waters entirely withdrew, the phase during which the deposition of the sulphides occurred had passed. The sulphides would then be acted upon by the hot waters and might form native copper and cuprite. Many, if not all, ferrous minerals present in veins and country rock would, in steam, tend to become oxidized, thus freeing some hydrogen which would then be available to help reduce copper oxides to the native metal. The presence of "limonite" does not necessarily mean that the alteration is supergene or formed by cold waters.[23]

The above statements are not advanced as arguments that all the native copper and cuprite formed, at Santa Rita, for example, are due to late post-sulphide hydrothermal alteration. This certainly is not the case. It does seem, however, as if the points brought out in these experiments may be used helpfully to explain the origin of part of the oxidized ores.

Bateman,[24] in a recent article concerning the ores of Northern Rhodesia, points out an example of oxidation of copper ores "several hundred feet below the present water level." The oxidized ores consist of copper carbonates, cuprite, tenorite, native copper, chrysocolla, and a few specks of sulphides. In some places unaltered chalcocite overlies these oxidized materials. Bateman explains this by means of a fluctuating ground water level; the deeper oxidation formed during an earlier geologic period of aridity, and by oxidizing waters travelling downward along inclined permeable strata beneath untouched sulphides. An occurrence of this kind might well mark the path of thermal waters. The most difficult thing to explain is the presence of malachite. Malachite is not, however, always present, and chal-

[22] Ballmer, J. G., personal communication.

[23] Gruner, J. W.: Hydrothermal Oxidation Experiments. ECON. GEOL., vol. 25, pp. 697–719, 1930. Tunell G., and Posnjak, E.: Discussion, Stability Relations of Goethite and Hematite, ECON. GEOL., vol. 26, pp. 337–343, 1931. Paper in press. Gruner, J. W.: Discussion, *idem*, vol. 26, pp. 442–445.

[24] Bateman, A. M.: The Ores of the Northern Rhodesia Copper Belt. ECON. GEOL., vol. 25, pp. 381–383; 391, 1930.

cocite and native copper may occur together in apparently contemporaneous mixtures. (*E.g.,* Mufulira, at a depth of 906 feet). Bateman considers that this copper might be hypogene, and compares it with Lake Superior ores.

The formation of native copper from the chlorides may be suggested to explain the origin of the Michigan copper deposits. The results would fit all the conditions known to the writer. These include the partial bleaching of hematite-containing rocks and also the presence of calcium chloride in the waters of some of the deeper mines.[25] Where H_2S was present in sufficient quantities, chalcocite would form. The fact that in all of the experimental work some copper oxides were obtained might, with good reason, be interpreted as evidence against the similar formation of the copper in the district under discussion, since only small amounts of cuprite have been reported in depth.[26] That native copper has been formed in the experiments is considered significant and it may be possible, by altering the conditions of the equilibrium, to do away with the formation of the oxides. As mentioned previously, any ferrous minerals present would tend to become oxidized and, by liberating hydrogen, help to reduce copper oxides.

In most, if not all, of the places in the Michigan copper deposits where hematite has been removed from near the copper, the iron would not have to migrate far in order to account for the bleaching. A movement of an inch or two would usually be enough and in many places less than this would suffice. It is thought that if copper was introduced in the form of a chloride, either CuCl or $CuCl_2$, there would be a reaction between the hematite and this chloride with the subsequent formation of metallic copper and ferric, or possibly ferrous chloride. The iron chloride could possibly move a short distance before being precipitated as the oxide.

The copper deposits of Coro Coro, Bolivia,[27] are similar in

[25] Butler, B. S., and Burbank, W. S.: The Copper Deposits of Michigan. U. S. Geol. Surv. Prof. Paper, 144, 1929.

[26] Butler, B. S., and Burbank, W. S.: *op. cit.*, pp. 134–135.

[27] Singewald, J. T.: Johns Hopkins Univ. Studies in Geology, No. 1, 1922.

many respects to those of Keweenaw Point but the geology is less complex. Native copper and some chalcocite and arsenides are found in a red sandstone in both bedded and vein deposits. Here, as in Michigan, the hematite near the ores has been removed. The same arguments concerning the origin of the Michigan copper deposits should hold in Coro Coro.

The copper deposits at Boleo, Mexico,[28] show much evidence of hydrothermal activity. Native copper is associated with zeolites well below the zone of oxidation and apparently independent of the sulphide ores. Some results of the present experiments might be of value in explaining the native copper in this area.

The results of certain experiments described in this paper may aid in the explanation of the origin of native copper in many lava flows.[29]

The transportation of copper compounds in alkaline solutions is believed to be a common process. Certain experiments described herein are of interest geologically because they show a way in which copper may be transported as a metal.

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[28] Touwaide, Marcel E.: Origin of the Boleo Copper Deposits, Mexico. ECON. GEOL., vol. 25, pp. 113–144, 1930.

[29] Butler, B. S., and Burbank, W. S.: *op. cit.*, pp. 142–145. This paper contains an excellent review of the literature on the copper occurrences associated with lava flows.

DEFORMATION OF GALENA AND PYRRHOTITE.

FRELEIGH FITZ OSBORNE AND FRANK DAWSON ADAMS.

INTRODUCTION.

In a series of experiments carried out between 1897 and 1910 it was shown by Adams that soft rocks, exemplified by alabaster and marble, as well as hard rocks, such as granite and diabase, under conditions of high differential pressure, could be deformed and made to flow. The former class underwent deformation by gliding or by twinning of the constituent mineral grains, whereas in the latter class, the movements took place by granulation, the resulting rock having the structure seen in nature in the augen gneisses. The two papers referred to below [1] were the first and last of a series published on this investigation and present the chief results obtained. After having studied the deportment of rocks under differential pressure a few experiments were carried out on the deformation of metallic minerals and other substances. Of these, three experiments were made with galena and pyrrhotite. It was found that these could be deformed. Galena behaved as the soft rocks, and the pyrrhotite as a hard rock. A description of these experiments, carried out in 1912, has not hitherto been published.

Quite recently Newhouse and Flaherty [2] have described the results of similar experiments on galena and sphalerite; however, their specimens were enclosed in copper and the maximum pressure was probably lower than that in the experiments described here.

[1] Adams, F. D. and Nicholson, J. T.: An Experimental Investigation into the Flow of Marble. Phil. Trans. Roy. Soc. London, Ser. A, vol. 195, pp. 963–401, 1901. Adams, F. D.: An Experimental Investigation into the Flow of Rocks. Int. Geol. Congress XI, C. R., pp. 911–945, 1910.

[2] Newhouse, W. H., and Flaherty, G. F.: Texture and Origin of Some Banded and Schistose Sulphide Ores. ECON. GEOL., vol. 25, pp. 603–604, 1930.

Method of Deformation.—The method of carrying out the experiments is described in both of the above-noted memoirs by Adams. A cylinder 1.57 inches long and .81 inch in diameter was turned and ground from the material to be tested. One end of the cylinder was .001 inch larger than the other and was made to slide into a hole drilled axially in a steel cylinder shown in Fig. 1–*A*, in which the walls of the central part have been reduced to .12 inch thickness. The hole was tapered in the same way as the specimen, and by heating the sleeve the specimen was allowed to slide in, to make perfect contact with the enclosing steel. Steel plungers were made to press on the ends of the specimen and the whole was placed in a powerful hydraulic press. The pressure was gradually increased and the amount of shortening measured by an extensometer. The reduced section in the sleeve was allowed to bulge until it showed signs of rupture, when the experiment was discontinued. After the deformation was complete the sleeve was milled off and the specimen examined.

Result of Deformation.—The result of the pressure is that the material flows out into the deformed part of the sleeve. The parts of the specimen contained within the unreduced parts of the block are unaffected except for a polish on the surface or a fracturing near the plunger. The specimen after the test appears as if two short cylinders terminated by cones,[3] whose apical angle varies with the material being tested, had advanced into the part where flowage had taken place. The result is that the movement of the material is outward from between the apices of the advancing cones.

GALENA.

The experiments were carried out on medium-grained galena from the Slocan District, B. C. The dimensions of the undeformed cylinders are shown in Fig. 1–*B*. Experiment 524 was carried out January 31, 1912; the enclosing block was made from nickel steel, and the wall at the reduced section was .120 inch in diameter. The experiment was at room temperature, the time of deformation was 1 hour, 35 minutes, and the maximum pres-

[3] These surfaces only approximate to cones.

sure was 97,500 pounds per square inch. As removed from the enclosing steel tube the bulge was seen to be not quite symmetrical and a faint vertical line of pulverized galena marked a place where the tube failed. The deformed column shows a polish absent on the undeformed specimen, and the polish is less marked on the bulged part than on the undeformed part.

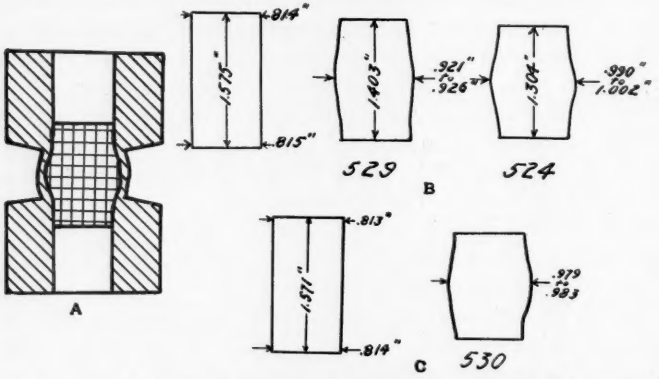

FIG. 1. *A*, diagrammatic cross section of deformed specimen contained in steel sleeve. The walls of the reduced section are .12 inch thick. *B*, dimensions of the undeformed and deformed galena specimens. *C*, dimensions of the undeformed and deformed pyrrhotite.

Experiment 529 was carried out in a tube of vanadium steel on similar galena. The tube ruptured at the end of one hour and before the galena was deformed to such an extent as in experiment 524. The polish was as in the previous experiment. The maximum pressure was 90,350 pounds per square inch.

Method of Investigation.—Vertical sections through the cylinder were sawed, ground, and polished. The polishing was done very lightly in order to avoid flowage of the surface layer. It was found that sections polished with considerable pressure did not etch to a structure. A number of experiments were tried to find a suitable etching reagent to bring out the structure in the galena. The electrolytic method suggested by Schneiderhöhn,[4]

[4] Schneiderhöhn, Hans: Anleitung zur mikroskopischen Bestimmung, etc., p. 117, 1922.

using a dilute solution of HCl, was tried and found to give good results with certain specimens but not with those being investigated. A three-per cent. solution of sodium acetate, using a weak current, and nitric acid alone diluted five to one, were found to suffer from the same disability. A paper by Stoicovici,[5] recently published, advocated again the old method used by Becke. The reagent is hydrochloric acid alone. He found the optimum concentration of acid is 17 per cent. This solution was tried and satisfactory etched surfaces were obtained on all specimens after several attempts. His time for etching was less than a minute. With these specimens five minutes were necessary. It is advisable not to withdraw the specimen from the HCl until the etching is complete, otherwise an uneven and spotted surface results. The effect observed on the specimen is due to two causes: the one is the different structures, and the other is the precipitation of lead chloride on the surface. The reaction is

$$PbS + 2HCl = PbCl_2 + H_2S.$$

A too heavy precipitate of lead chloride may be dissolved with hot water. A cube of galena from the Joplin district was used in testing the etching methods. It did not etch homogeneously but became divided into a series of irregular lamellæ, which on the cube face appear parallel to the trace of the octahedral axis and tend to divide the cube face into four parts. Large specimens in the Redpath Museum show similar structures which have been attributed to the variation in rate of growth during the final stages and explained as the threefold reflection from the octahedral face of alum, found by Miers[6] when growing the crystals in solution in his suspended goniometer. However, similar structures were found in sections cut through the centers of "crystals" and similar differences in the orientation of the laminæ noted. Fig. 2 is an attempt to show this in a hand specimen of galena cut

[5] Stoicovici, Eugen: Salzsaure als Atzmittel für Bleiglanz. Zeit. f. Cryst., 76, pp. 310–314, 1931.

[6] Miers, H. A.: An enquiry into the variation of angles in crystals, especially of potassium-alum and ammonium-alum. Phil. Trans. Roy. Soc. London, Ser. A, vol. 202, pp. 459–523, 1903.

nearly parallel to 100. The difference of orientation of adjacent grains is too small to be accounted for by twinning and must be the result of gliding with slight rotation.

The lamellæ resemble those produced by deformation, so they were examined critically. It was surprising to find such a structure on crystals from the Joplin district, especially those which now project into open spaces and are commonly considered not to have undergone deformation. It is possible that the galena was surrounded by some mineral which transmitted stresses to them and was later dissolved. If they grew into open spaces, differential expansion due to change in pressure after the formation of the galena is the only force able to produce the observed deformation. Tutton [7] states that the thermal expansion of cubic crystals is the same in all directions. If the crystal grew under hydrostatic pressure it might be deformed on release, due to the differences in the compressibility along the cubic and octahedral axes. Fluorite,[8] also isometric, shows marked difference in compressibility in these directions, and some fluorite crystals are similarly marked. The structures of the Joplin galena are due to a slight change in orientation and appear similar on etching to those developed on deformed specimens, making the interpretation of the polished surface of the deformed galena somewhat uncertain and introducing the possibility of overestimating the amount of movement due to pressure.

The Undeformed Specimens of Galena.—It is noteworthy that the specimens chosen for deformation are from the Slocan District, British Columbia, and are gneissic. In the earlier experiments attempts were made to cut cylinders from other galena. but they broke. It was only when the specimens were cut from the Slocan gneissic material that they were coherent. This illustrated one important property of the gneissic galena, that of toughness. In most of the specimens examined the blades of the etched structure are parallel, but where twinning is prominent the etching pattern following the cleavage gives a herring-bone

[7] Tutton, A. E. H.: Crystallography and Practical Crystal Measurement, p. 1303, 1922.

[8] Niggli, Paul: Lehrbuch der Mineralogie, I, p. 189, 1920.

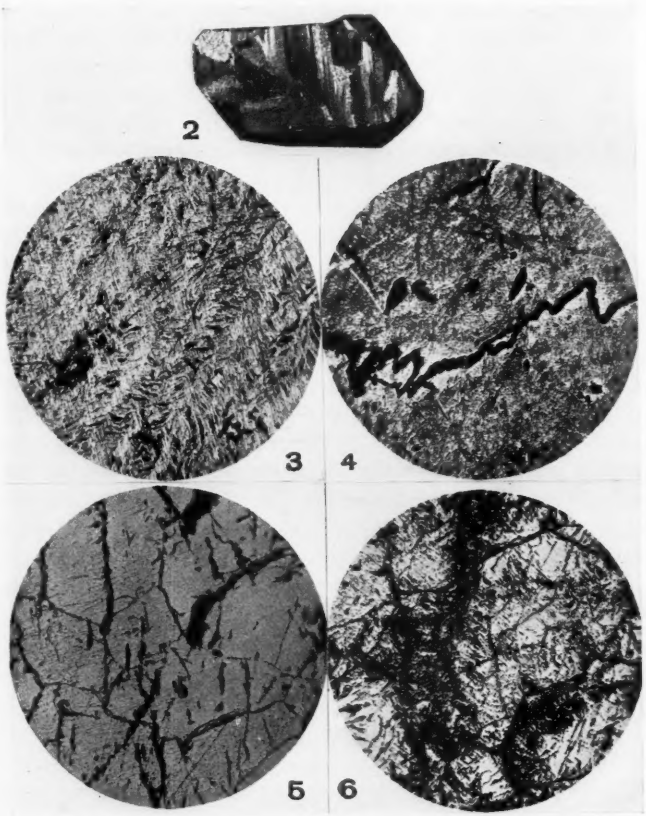

FIG. 2. Galena from Joplin showing lamellæ on 100. × 1.

FIG. 3. Etched surface of gneissic galena from the Slocan used in the experiments. × 20.

FIG. 4. Heavily etched section of deformed galena. The black line is a calcite vein etched out. In the undeformed parts of the specimen the vein is straight. × 20.

FIG. 5. Undeformed pyrrhotite. The pitted sections are near 0001. X 20.

FIG. 6. Deformed pyrrhotite showing the fracturing. × 20.

effect (Fig. 3). However, the appearance suggests that gliding rather than twinning was important in the yielding in the deformation. The galena contains some grains of sphalerite which appear unaffected by the deformation, and also contains minute grains of argentite, seen on etching with hydrogen peroxide.

Deformed Galena.—The two deformed specimens were cut from the gneissic galena with the cylinder axis parallel to the direction of the gneissic structure. In the less deformed specimen, number 529, the original gneissic structure is easily visible in the undeformed ends. In the central part, the older gneissic structure has been obliterated, and the structure is massive. The outline of the grains is amœboid, resembling some crystalline limestone or quartzite. The texture is quite distinct from the normal granular pattern of undeformed galena. Examination of the equidimensional grains shows twinning and gliding planes, but they are less numerous in any one grain than in the undeformed grains; however, the grains are smaller than in the original specimen. In some places the equidimensional character suggests re-crystallization, but the evidence of specimen 524 shows it is only a stage in the deformation.

Specimen 524 was more deformed and shows the similar amœboid texture on the surfaces near the cones of no deformation, but in the central part, where the flowage was greatest, the new gneissic structure crosses the older gneissic structure and obliterates it. The grain is, of course, much finer than in the original rock, and the mineral aggregate shows evidence of gliding and twinning.

Either of the deformed specimens appears to be as strong transverse to the length as the original.

PYRRHOTITE.

Experiment 530 was carried out on a column of pyrrhotite from the Centre Star Mine at Rossland, B. C.; the enclosing tube was of nickel steel similar to that employed in experiment 524, and the time was 2 hours, 35 minutes. The maximum pressure was 192,000 pounds per square inch. The ends next

the plungers show fracturing, giving flat lens-shaped plates, which break out readily and make it impossible to measure the height of the deformed cylinder. The outlines and dimensions of the test piece and the undeformed specimen are shown in Fig. 1–*C*. The body of the cylinder shows vertical striations and a high polish, which is less perfect on the bulged part. The bulged part is marked by Luder's lines inclined about 45° to the vertical axis of the cylinder. Although the contained angle is nearly 90° as nearly as can be observed, the vertical axis appears to bisect the smaller angle between the lines.

Undeformed Pyrrhotite.—The specimen is an equigranular aggregate of pyrrhotite anhedra with a few irregular and interstitial grains of chalcopyrite and some calcite and silicious material. Tests with polarized light show that the aggregate is almost untwinned. In a few grains somewhat irregular ribbons were observed resembling irregular twinning, but they may be due to intergrowth of two minerals. The 0001 sections of the pyrrhotite are recognized by the fact that they polish to a pitted surface when the other sections are already smooth. The pitted surfaces are seen to be isotropic with polarized light. According to Dickson,[9] the composition of the Rossland pyrrhotite corresponds to the formula Fe_8S_9. In order to determine the orientation of given sections of the mineral, a crystal of pyrrhotite from Elizabethtown, Ontario,[10] was selected and 12 facets ranging from the basal to the vertical zone were ground and polished on it. This pyrrhotite approximates to the same formula as that from Rossland. It was found that the basal section tends to polish to a somewhat pitted surface and to be isotropic, and that the face in the prism zone shows the maximum rotation of the plane of polarization when the basal parting makes an angle of 45° with the vibration directions of the polarizer. The maximum rotation observed and measured, using a Bertrand ocular with a Vernier analyzer, was one degree. The other sections give a

[9] Dickson, C. W.: The Ore Deposits of Sudbury, Ontario. Trans. A. I. M. E. 34, p. 24, 1904.

[10] Harrington, B. J.: On the Composition and Mode of Occurrence of the Pyrrhotite from Elizabethtown, Ont. Amer. Jour. Sci., (3) vol. 11, pp. 387–388, 1876.

lower maximum rotation, and the amount of the rotation varies roughly with the angular distance from the 0001 face. Repeated observations failed to give sufficiently accurate values so that the variation in the rotation with the orientation could be worked out. This is possibly owing to the small size of the facets and the difficulty of mounting them normal to the line of collimation. However, it is possible to determine approximately the prismatic and the basal section.

Deformed Specimens.—The deformed sections of the pyrrhotite are unlike the deformed galena sections in that they are much weaker. The ends next the plunger tend to crack and that next to the cones of no distortion is similarly cracked. The central deformed part is not cracked but is weaker transversely than the undeformed specimens although of larger cross-section. The microscopic examination shows that the grains have yielded by marginal brecciation. The grains in the deformed section are largely surrounded by zones of broken pyrrhotite, which tends to polish out as channels. This brecciated zone contains small grains of recognizable pyrrhotite, but most of it is too finely divided to make out the individual grains. The unbrecciated grains show a tendency to fracture. The fractures are irregular or follow the cleavage or parting. No traces of new twinning or parting planes are to be found that can be ascribed to the deformation.

The mode of yielding resembles that of the silicate rocks and of some metals. The aggregate is coherent due to the interlocking of the mineral fragments in the "mylonitized" zone surrounding the pyrrhotite anhedra. That such a mode of deformation may be present in a specimen which remains coherent is not surprising when it is considered that cast-iron filings may be made into briquets by pressure.

SUMMARY.

The result shows that the gneissic structure may be produced by deformation in galena, and that the deformed galena is tougher than the original. The flowage is by gliding and twinning, as in

alabaster and marble. Certain similar lammellar structures in galena may not be due to deformation. On the other hand, similar deformation of pyrrhotite caused the margins of the grains to be broken and the aggregate to be held together with this cement. The manner of flowage is, therefore, similar to that in the silicate rocks. As might be expected, a much greater pressure is required to make pyrrhotite flow than galena. Approximately twice the pressure was required to reduce the length of the cylinder of pyrrhotite the same amount as the cylinder of galena.

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DISCUSSION AND COMMUNICATIONS

THE STABILITY RELATIONS OF GOETHITE AND HEMATITE.

Sir:—In an article entitled "The Stability Relations of Goethite and Hematite"[1] we stated our belief that a conclusion of J. W. Gruner published in his article entitled "Hydrothermal Oxidation and Leaching Experiments; Their Bearing on the Origin of Lake Superior Hematite-Limonite Ores," and based on experiments carried out by him, is erroneous, and we stated the experimental data on which our belief rests. This conclusion of Gruner is as follows:

> It is probable, however, that as Van Bemmelen pointed out long ago, limonite is stable in the presence of water and under corresponding pressures at temperatures which approach 300° C.[2] . . . Limonite is stable at 250° C. in the presence of water and steam at corresponding pressures.[3]

Experiments carried out by Gruner more recently[4] indicate, according to him, that "goethite is unstable at these temperatures [250° C. and 300° C.], as well as at 200° C." This brings Gruner nearly into agreement with us, as we[5] stated that from the investigation of the system, Fe_2O_3–SO_3–H_2O, by Posnjak and Merwin

> it must be concluded that goethite is unstable at temperatures not much above 140°. Thus the temperature 130° was given in the published report as the approximate location of the transition temperature of $Fe_2O_3 \cdot H_2O$ (goethite) to Fe_2O_3 (hematite) in the binary system, Fe_2O_3–H_2O. To fix brackets for the transition point is very difficult,

[1] ECON. GEOL., vol. 26, pp. 337–343, 1931.
[2] ECON. GEOL., vol. 25, p. 715, 1930.
[3] *Op. cit.*, p. 864.
[4] ECON. GEOL., vol. 26, p. 443, 1931.
[5] *Op. cit.*, p. 338.

but the narrowing of the $Fe_2O_3 \cdot H_2O$ (goethite) and Fe_2O_3 (hematite) fields in the ternary system shows that the transition temperature in the binary system cannot be very far from 130°.

It is emphasized that in all of the statements made by us it has been set forth very clearly that this location of the transition point, $Fe_2O_3 \cdot H_2O$ (goethite), Fe_2O_3 (hematite), solution, vapor, in the binary system, Fe_2O_3–H_2O, is approximate; it is not a precise determination such as, for example, that of the transition point, $Na_2SO_4 \cdot 10H_2O$, Na_2SO_4, solution, vapor, in the binary system, Na_2SO_4–H_2O, by Richards and Wells.[6]

The method of determination of the transition point in the binary system, Fe_2O_3–H_2O, used by Posnjak and Merwin is not, however, open to the objection advanced by Gruner.[7] This method is one devised to get around the extreme difficulty of establishing equilibrium in systems in which the solubilities are extremely low; for example, the binary system, Fe_2O_3–H_2O. The method consists in the treatment of the binary system as a limit in a ternary system in which the solubilities are greater owing to the presence of the third component. Thus the transition temperature of $Fe_2O_3 \cdot H_2O$ (goethite) to Fe_2O_3 (hematite) in the binary system, Fe_2O_3–H_2O, was determined by short extrapolation of the *boundary curves* of the goethite and hematite fields in the ternary system, Fe_2O_3–SO_3–H_2O. It does not follow that a different value would have been assigned to this transition temperature by extrapolation of the boundary curves of the goethite and hematite fields in the ternary system, Fe_2O_3–HCl–H_2O, as compared with the ternary system, Fe_2O_3–SO_3–H_2O. The transition temperature of $Fe_2O_3 \cdot H_2O$ (goethite) to Fe_2O_3 (hematite) in the binary system, Fe_2O_3–H_2O, is an *invariant point*, and in all ternary or poly-component systems of which the binary system, Fe_2O_3–H_2O, is a part, the location of this invariant point must be the same according to the phase rule.

In the binary system, Na_2SO_4–H_2O, equilibrium is attained in a period of minutes or hours and a direct determination of the transition point of $Na_2SO_4 \cdot 10H_2O$ to Na_2SO_4 was carried out

[6] Richards, T. W. and Wells, R. C.: Zeit. physik. Chem., 43, p. 465, 1903.

[7] Econ. Geol., vol. 26, p. 443, 1931.

by Richards and Wells very precisely. This method is not applicable, however, in the case of the binary system, Fe_2O_3–H_2O, due to the extreme slowness of attainment of equilibrium. The method of extrapolation of boundary curves in the ternary system, Fe_2O_3–SO_3–H_2O, was therefore employed because of the possibility of more rapid establishment of equilibrium in the ternary system.

In the majority of investigations of heterogeneous equilibria the binary systems bounding the ternary system under consideration have been mapped before the ternary system itself. That is, the simple systems have usually been mapped before the more complex ones. However, several systems have been studied by different investigators in which it has been advantageous to reverse this procedure and work back to the simple system as a limit in a system of a larger number of components, owing to the greater difficulty of attaining equilibrium in the simple system. The system, Fe_2O_3–H_2O, is one of these.

No misunderstanding should have arisen from the statement in our paper [8] that:

> the use of the term "limonite" by Gruner in a detailed physico-chemical and geological investigation of iron ores is open to criticism, since at the present time this term is generally used by mining geologists and members of the U. S. Geological Survey and of the Geophysical Laboratory to denote unidentified ferric precipitates including hematite, goethite, lepidocrocite, jarosite, etc., and has sometimes been used by members of the Geophysical Laboratory to denote fine-grained aggregates of ferric oxide monohydrate (goethite). There is no mineral species, limonite; the formulas given under this name in mineralogies are erroneous.

Gruner [9] has replied that:

> It seems to me that this criticism is not justified, for the material I used was not much closer to $Fe_2O_3 \cdot H_2O$ in composition than the material usually called limonite. . . . I doubt whether it will be possible to dispense with such convenient terms as limonite in the case of extremely fine-grained mixtures of ferric hydroxide with SiO_2 and other compounds.

As our statement just quoted indicates, we do not suggest that

[8] *Op. cit.*, p. 337.

[9] ECON. GEOL., vol. 26, p. 444, 1931.

the term limonite should never be used. It can only be used, however, as a convenient field name for undetermined ferric minerals since it has been shown that no compound, limonite, exists of the composition formerly given in mineralogies. The term limonite is employed as such a field name for undetermined ferric minerals by Spencer,[10] Ransome,[11] Locke,[12] Blanchard and Boswell,[13] and Short,[14] with explicit statements that they use it in this sense only, and in field work we have followed this custom for some time.

Our criticism relates to Gruner's use of the term limonite in the statement of stability relations (quoted again at the beginning of the present discussion) of mixtures of undetermined, or unspecified substances where, obviously, it has no meaning. In physico-chemical and petrographic investigations the minerals should be determined and specified. We pointed out that it is now possible to determine hematite, goethite, and lepidocrocite by optical or X-ray methods. In his most recent work Gruner himself has carried out such determinations.

Gruner[15] originally stated that his experiments "lend strong support to the hypothesis that the Lake Superior hematite-limonite ores were oxidized and leached hydrothermally. It is thought that great basic Keweenawan intrusions associated with the Lake Superior geosyncline were the sources of heat and solutions necessary for the ore concentrations." More recently he[16] has written:

> The probability that goethite is unstable above 140° C. does not imply, however, that those Lake Superior ores containing limonite were concentrated by weathering, but it indicates that the temperatures were prob-

[10] Spencer, A. C.: "The Geology and Ore Deposits of Ely, Nevada." U. S. Geol. Survey Prof. Paper 96, p. 101, 1917.

[11] Ransome, F. L.: "The Copper Deposits of Ray and Miami, Arizona." U. S. Geol. Survey Prof. Paper 115, p. 136, 1919.

[12] Locke, Augustus: "Leached Outcrops as Guides to Copper Ore," p. 167. Williams and Wilkins, Baltimore, 1926.

[13] Blanchard, Roland and Boswell, P. F.: ECON. GEOL., vol. 20, p. 615, 1925.

[14] Short, M. N.: "Microscopic Determination of the Ore Minerals." U. S. Geol. Survey Bull. 825, p. 104, 1931.

[15] ECON. GEOL., vol. 25, p. 864, 1930.

[16] ECON. GEOL., vol. 26, p. 445, 1931.

ably somewhat lower than 200° C. as was originally stated. . . . Though it is probable that goethite is not stable above 140° C. it is possible that it can form and exist for long periods as a metastable product somewhat above this temperature ("formation fields and existence fields" of Tunell and Posnjak). This might very well be the case in the decomposition of ferrous silicates like greenalite, which perhaps takes place in a number of complicated steps.

To maintain the hypothesis that the deposits containing goethite formed above 140° C., Gruner now has to assume that the goethite formed and persisted above its maximum stability temperature. Inasmuch as the formation or persistence of goethite above its range of stability during an unknown lapse of geologic time cannot be, or at least has not been, verified by Gruner's laboratory experimentation, it is obviously purely an assumption. This assumption could have been made just as well in the beginning without recourse to equilibrium experiments.

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STANNOUS CHLORIDE, AN ETCHING REAGENT FOR IRON ORES

Sir:—In a study of polished specimens from Cornwall, Pa., I investigated several etching reagents in order to obtain a suitable one to distinguish readily between the iron oxides, and to bring out the structure of magnetite. I found that stannous chloride gave the best results and thought it might also be of interest to others.

This etching solution is made by dissolving stannous chloride in hydrochloric acid (1–1 dilution). The solution is applied to the surface by means of a platinum wire and allowed to remain there for three minutes. It is then dried and the spot immediately washed with distilled water. The washing should follow immediately after the drying in order to prevent a difficultly removable brownish stain from forming. After etching, the surface may need to be gently rubbed in order to remove any stain present.

This reagent serves a double purpose: it brings out the structure of magnetite and it serves to differentiate between some of the iron-bearing minerals. The list that follows shows its effect on some of them. It is negative to:

Chalcopyrite	Cornwall, Pa., Sudbury.
Pyrite	Cornwall, Pa., Adirondacks.
Hematite (specularite)	Cornwall, Pa., Adirondacks, Jackson Mt., Marquette.
Ilmenite	Adirondacks, Ivry Mine, Quebec.
Pyrrhotite	Sudbury.
Sphalerite	Cornwall, Pa.

It reacts with:

Goethite	Rio Tinto, Spain.
Martite	Lake Superior Region.
Magnetite	Cornwall, Pa., Adirondacks, Ivry Mine, Quebec.

Some comment should be added respecting the minerals with which it reacts. The goethite is strongly attacked, with the formation of deep pits and the removal of the polish. The reaction on martite is interesting but as only two specimens were examined the results may not be conclusive. These specimens upon etching became stained brown and showed evidence of some slight irregular solution along some small cracks. Why the reagent should react with martite and not with hematite is puzzling.

The etching reaction on magnetite is complicated by the presence of more than one kind of magnetite. Three distinct varieties of magnetite were found in the Cornwall ores. The normal and most abundant variety etches in less than three minutes. However, for the development of the best structure, one to one and a half minutes was found most satisfactory, and in only a few cases was as long as three minutes required. (Figs. 1 and 2.)

Newhouse and Callahan[1] have noted in the ore at Cornwall two varieties of magnetite which are so similar that they can only be told apart when they occur in the same specimen. (Figs. 3 and 4.) They state that the one that is bluish and harder is normal magnetite, whereas the other, which is brownish and

[1] Newhouse, W. H. and Callahan, W. H.: Two Kinds of Magnetite. ECON. GEOL., vol. 22, pp. 629–632, 1927.

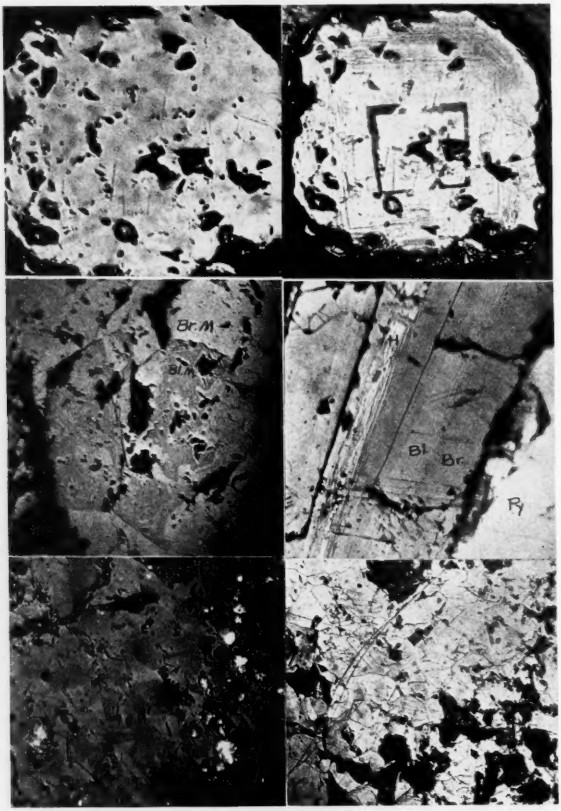

FIG. 1. Polished section of magnetite, single grain. × 70.

FIG. 2. Same as Fig. 1, etched with stannous chloride solution for two minutes.

FIG. 3. Brown magnetite (Br.M.) replacing blue magnetite (Bl.M.). × 145.

FIG. 4. Hematite (H) replaced by blue magnetite (Bl.), which is replaced by brown magnetite (Br.). × 145.

FIG. 5. Anisotropic magnetite. Crossed nicols. × 70.

FIG. 6. Anisotropic magnetite, etched 90 seconds, showing grain boundaries. Same specimen as Fig. 5.

softer, corresponds with the artificially produced ferromagnetic ferric oxide of Sosman and Posnjak.[2] On the other hand, Schneiderhöhn and Ramdohr[3] consider that the harder bluish variety, which they call maghemite, is the ferromagnetic ferric oxide, and that the softer brownish variety is the normal magnetite. The writer has been unable to isolate either one for chemical analysis. Fig. 4 shows hematite being altered to the bluish variety of magnetite which in turn is being altered to the brownish variety. The bluish variety is more slowly etched than the brownish and in this respect it is also intermediate between the brownish variety and hematite.

The third variety of magnetite is anisotropic and seems to bear no relation to those mentioned above. Its areal distribution differs, and in one specimen both the bluish and the brownish magnetite were seen to be anisotropic. Chemical analysis shows it to contain abundant ferrous iron, so it is not weakly anisotropic hematite. On etching, this variety is seen to be composed of polygonal grains the boundaries of which appear after 90 seconds. (Figs. 5 and 6.)

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[2] Sosman, R. B. and Posnjak, E.: Ferromagnetic Ferric Oxide, Artificial and Natural. *Jour. Wash. Acad. Sci.*, vol. 15, no. 14, pp. 329–342, 1925.

[3] Schneiderhöhn, H. and Ramdohr, P.: Lehrbuch der Erzmikroskopie, vol. 2. P. 536. G. Borntraeger, Berlin, 1931.

REVIEWS

Mineralische Bodenschätze im Südlichen Afrika. By H. SCHNEIDERHÖHN. Mit Beiträgen über die Diamantlagerstätten Südafrikas, by E. KAISER, and die Kohlenvorkommen Südafrikas, by P. KUKUK. Pp. viii + 111, figs. 114. N. E. M. Verlag, Berlin, 1931. Price, 18 M.

This remarkably well illustrated account of the mineral deposits of South Africa is an excellent summary of the geological phenomena observed during the excursions of the members of the 15th International Geological Congress.

Dr. Schneiderhöhn gives a summary of the knowledge that has accumulated concerning the geology of many of the more important deposits in southern Africa, and has in many instances added to this knowledge as the result of his own observations. It is impossible to summarize satisfactorily such a comprehensive and at the same time such a condensed account as the author has given us. It is sufficient to state that the geological environment of each of the deposits visited is clearly portrayed and their character is concisely discussed. Some of the discussions are particularly noteworthy for their thoroughness, such as those of the Tsumeb mine and the diamond-bearing areas, in Southwest Africa, the deposits in the Bushveld Complex, the coal resources of the Union of South Africa and the copper deposits in Northern Rhodesia. Besides, there are brief descriptions of the other ores of Northern Rhodesia and those of Southern Rhodesia and of Katanga:

The summaries are based mainly on the work of the South African geologists, but there are many significant comments by Schneiderhöhn which are of special interest. He, for instance, declares his profound conviction that the Witwatersrand gold is a metamorphosed placer deposit in a fan conglomerate.

The paper is richly illustrated with maps, sections and reproductions of photographs, most of which are new.

W. S. BAYLEY.

Earth Features and Their Meaning: An Introduction to Geology. By W. H. HOBBS. 2d edition. Pp. 517, figs. 508. Macmillan, New York, 1931. Price, $4.50.

In the needed revision of this widely known book, considerable new material has been added, other material has been brought up to date, many new figures have been added, and the reading references have been revised. The chapter headings all remain the same as in the earlier edition

but two new chapters have been added, namely, Chapter 32, "The Earth's Atmosphere Envelope," and Chapter 33, "Eddies of the Atmosphere." The size has been increased by 12 pages. The main body of the text, however, does not appear to have been revised as much as the advance in the science would warrant. It will, however, continue to fill the valuable place that the earlier edition made for itself both for the general reader and as a reference and collateral reading for the student.

ALAN BATEMAN.

Simple Determinative Mineralogy. By H. R. BERINGER. Pp. ii + 239. Mining Publications, Ltd., London, 1931. Price, 10s. 6d.

Beringer's new book, which may be regarded as a revised edition of his "Mineral Determination" published some years ago, is based on the differences in specific gravity exhibited by pure minerals. It is intended not only for college use, but also for the use of prospectors.

The author introduces his volume by descriptions of simple methods of obtaining clean specimens by sifting, jigging, vanning, panning, and concentrating by the aid of magnets, and follows with a statement of the best methods of determining specific gravity.

The main portion of the book consists of three parts. The first is a list of about 800 minerals grouped in the order of their specific gravities and arranged in each group in order of hardness. The second part consists of brief descriptions of the physical properties and characteristic chemical properties of the same minerals arranged in order of specific gravities, and the third is a condensed account of the characteristic reactions of the chemical elements found in minerals. In the case of the less common elements, the names of the minerals in which they occur are given.

The book attacks the problem of determining the nature of an unknown mineral in a way that has not hitherto been generally employed.

W. S. BAYLEY.

Elements of Geology. By W. J. MILLER. Pp. 495, figs. 330. D. Van Nostrand Co., New York, 1931. Price, $3.00.

This elementary text, intended for a one-term course in general geology, is an abridgement of the author's two previous volumes, entitled "Introduction to Physical Geology" and "Introduction to Historical Geology." The subject matter and general arrangement of material follow that of the larger texts. Part I, Physical Geology, occupies 271 pages, and Part II, Historical Geology, 205 pages.

The condensation has been carried out satisfactorily and the book is written in an interesting style. It is profusely illustrated but unfortunately the halftones are so poorly reproduced that many of them are

almost useless. A better surfaced paper would have made the well-chosen pictures more vivid. A lack of block diagrams is regrettable.

The volume should serve as a very satisfactory text where an abbreviated course in general geology is desired. Teachers of such courses should give it serious consideration.

ALAN BATEMAN.

BOOKS RECEIVED.

BY

DAVID GALLAGHER.

Research Council of Alberta, Eleventh Annual Report, 1930. Pp. 76, Report No. 26, Edmonton, 1931. Account of recent work, fuels, water, road metal, soils.

Uganda Geological Survey, Annual Report, for year ending Dec. 31, 1930. By E. J. WAYLAND, et al. Pp. 43, pl. 1. Entebbe, 1931. Price, 3/. Year's work, short papers, sketch map of Uganda geology.

Geology and Ore Deposits of Rouyn-Harricanaw Region, Quebec. By H. C. COOKE, W. F. JAMES, AND J. B. MAWDSLEY. Pp. 314, maps. Can. Geol. Surv. Mem. 166, Ottawa, 1931. Price, 45 cts. General geology of the area, Keewatin and Timiskaming series, structure, intrusives, etc., and economic geology including descriptions of the numerous mines and claims.

Fort William and Port Arthur, and Thunder Cape Map-areas, Thunder Bay District, Ontario. By T. L. TANTON. Pp. 222, maps. Can. Geol. Surv. Mem. 167. Ottawa, 1931, 30 cts. General geology of the region, and descriptions of the mines, especially the Thunder Bay silver area.

Illinois State Geological Survey, Papers Presented at Quarter-Centennial Celebration. Pp. 300. Ill. Geol. Surv. Bull. 60. Urbana, 1931. Papers on: History of Geological Investigations in Illinois, Research Needs of the Illinois Coal Industry, Studies Relating to the Order and Conditions of Accumulation of the Coal Measures.

Geology of Jefferson County, Ohio. By R. E. LAMBORN. Pp. 304, maps. Geol. Surv. of Ohio, 4th series, Bull. 35, Columbus, 1930. Particularly detailed stratigraphy.

Geology of the Eastern Part of the Santa Monica Mountains, Los Angeles County, Calif. By H. W. HOOTS. Pp. 134, excellent maps. U. S. Geol. Surv. Prof. Paper 165–C, Washington, 1931. Price, 75 cts. Particularly full description of the stratigraphy and fossils.

The Significance of Geological Conditions in Naval Petroleum Reserve No. 3, Wyoming. By W. T. THOM, JR., AND E. M. SPIEKER,

with a section on the Waters of the Salt Greek-Teapot Dome Uplift, by H. Stabler. Pp. 64, maps, production graphs, illustrations. U. S. Geol. Surv. Prof. Paper 163, Washington, 1931. Price, $1.25. Geology, with data on safety as a reserve, and estimated oil content.

A Syllabus of Pennsylvania Geology and Mineral Resources. By G. H. ASHLEY. Pp. 159, maps, illustrations. Topog. and Geol. Survey Bull. G–1, Dept. of Internal Affairs, Comm. of Penn. Harrisburg, 1931. Popular presentation of principles of geology, general geology of Penn., and State mineral production statistics.

The Wasatch Plateau Coal Field, Utah. By E. M. SPIEKER. U. S. Geol. Surv. Bull. 819. Pp. 210, maps, illustrations, and many columnar sections. Washington, 1931. Price, $1.30. General geology of the region, exposition of the properties of the coal, and description of the individual areas.

Relationship Between Oxidizability and Composition of Coal. By W. FRANCIS AND H. M. MORRIS. U. S. Bur. Mines, Bull. 340, pp. 44. Washington, 1931. Price, 10 cts.

Report of the Committee on Sedimentation for 1929–1930. W. H. TWENHOFEL, Chairman. National Research Council, Div. Geol. and Geog., Repr. and Circ. Series, No. 98, Washington, 1931, pp. 97. Price, $1.00. Contains several valuable papers.

The Kaolin Minerals. By C. S. ROSS AND P. F. KERR. U. S. Geol. Surv. Prof. Paper 165–E, pp. 29, Washington, 1931. Price, 15 cts. The mineralogy of this difficult group cleared up and specifically described.

Gerland's Beiträge zur Geophysik: Ergänzungshefte für Geophysik. Band I, Heft. 1–4. Pp. 471. Edited by V. CONRAD, J. KOENIGSBERGER, AND H. REICH. Akad. Verlagsgesellsch. M. B. H., Leipzig, 1931. A new journal devoted to geophysics, of which four numbers have already appeared, with excellent contributions from prominent geophysicists throughout the world.

The Mineral Industry, Vol. XXXIX: Statistics, Technology and Trade, 1930. G. A. ROUSH, editor. Pp. xvi + 816. McGraw-Hill Book Co., New York. Price, $12.00.

Copies of books mentioned under "Reviews" or under our "New Book List" (see advertisement page) may be purchased through our Journal Bookshop by writing to W. S. Bayley, University of Illinois, Urbana, Ill.

SOCIETY OF ECONOMIC GEOLOGISTS

Eleventh Annual Meeting at Tulsa.—The eleventh annual meeting and technical session of the Society of Economic Geologists will be held in Tulsa, Oklahoma, on December 29–31, 1931, at the invitation of the American Association of Petroleum Geologists and in conjunction with that Society, the Geological Society of America, and its affiliated societies. The headquarters of the various organizations will be the Mayo Hotel and all technical sessions will be held there.

Technical Sessions.—The Society will hold a joint meeting with the American Association of Petroleum Geologists and the Geological Society of America at which papers dealing with broad problems of the petroleum industry will be presented. The address of the retiring President, L. C. Graton, on the subject, "The Depth-Zones in Ore Deposition," will be given in joint session with the Geological Society of America. A separate technical session of the Society will also be held and it is planned to have a limited number of papers with ample time for discussion.

Program Committee.—The following committee is in charge of the technical program: W. T. Thom, Jr., chairman (address, Guyot Hall, Princeton, New Jersey), E. S. Moore, Sidney Powers and G. R. Mansfield. Those wishing to present papers before the Society should address a member of the committee. A limited number of papers by non-members will be accepted.

Field Trips.—Arrangements are being made for field trips before and after the meetings as follows:

Trip 1. Dec. 28. Tulsa—Spavinaw. Uncovered "buried hills."
Trip 2. Dec. 28. Tulsa—Oklahoma City. Oil field problems.
Trip 3. Dec. 31–Jan. 2. Arbuckle Mountains and Ardmore Basins. Structure and Stratigraphy.
Trip 4. Jan. 2–4. Ouachita Mountains. Structure and Stratigraphy.
Trip 5. Jan. 3–4. Wichita Mountains. Structure and Stratigraphy.

A special trip is being arranged following the meetings for members of the Society of Economic Geologists and guests to the recently discovered quicksilver deposits of Arkansas, and also to Magnet Cove, and perhaps to the diamond field.

The Society's circular letter of November 23 stated that the Oklahoma City field trip was arranged for December 27. This should read December 28.

NEW MEMBERS.

The following have been elected to membership in the Society:

H. B. Aldrich, Madison, Wisconsin
L. P. Barrett, Pittsburgh, Pennsylvania
J. Mackintosh Bell, Almonte, Ontario
H. C. Boydell, Toronto, Ontario
G. C. Branner, Little Rock, Arkansas
C. S. Corbett, New York City
Donald Davidson, Chambishi, Northern Rhodesia
J. T. Duce, New York City
A. F. Duggleby, New York City
C. R. Fettke, Pittsburgh, Pennsylvania
G. M. Fowler, Joplin, Missouri
L. I. Grange, Wellington, New Zealand
J. E. Hawley, Kingston, Ontario
E. T. Hodge, Eugene, Oregon
R. J. Holden, Blacksburg, Virginia
M. E. Hurst, Toronto, Ontario
W. B. Jewell, Nashville, Tennessee
E. S. Larsen, Cambridge, Massachusetts
T. F. Lundberg, New York City
Montague Ongley, Wellington, New Zealand
R. J. Parker, London, England
D. B. Reger, Morgantown, West Virginia
E. H. Sellards, Austin, Texas
D. C. Sharpstone, Luanshya, Northern Rhodesia
J. D. Sisler, Morgantown, West Virginia
J. Ellis Thomson, Toronto, Ontario
George Tunell, Washington, D. C.
B. H. Van Der Linden, The Hague, Holland
J. W. Vanderwilt, Washington, D. C.
W. F. Walker, Oroya, Peru

Political and Commercial Geology Scholarships.—Another award amounting to $350 will be made immediately or for next year, out of the funds accrued in royalties on the sale of "Political and Commercial Geology," edited by J. E. Spurr (McGraw-Hill). On the title page of this book is the statement: "Royalties received from the sale of this book will be assigned to an institution of learning to finance further studies along the lines followed in the volume." The award will be made without regard to other fellowships or financial support which applicants may have. Requests for information and applications giving qualifications should be sent to the chairman of the committee, Dr. E. C. Harder, 2900 New York Central Building, New York City.

SCIENTIFIC NOTES AND NEWS

D. D. Irwin, general manager of the Roan Antelope Mines, Northern Rhodesia, sailed from New York on November 20, and after a stop in London, will reach Rhodesia on January 8.

Richard N. Hunt, recently of Santa Barbara, now resides in Los Altos, Calif. He has been spending some weeks in Mexico, returning home late in November.

H. Foster Bain, secretary of the A. I. M. E., has resigned his position to take up the managing directorship of the Copper and Brass Research Association in a five-year program of research to extend the technical uses of copper and brass.

T. M. Broderick, chief geologist of the Calumet & Hecla Mining Company, has been appointed research professor of geology at the Michigan College of Mining and Technology, and will retain his present position but devote part of his time to research work on utilization of low-grade iron ores.

Anton Gray will not return to the Mufulira Mine, Northern Rhodesia, for some time. His headquarters will be at the London office, Selection Trust Building, Coleman St., London.

A. A. Levensaler, formerly of the American Smelting and Refining Company, has opened offices as a consulting engineer at Seattle, Wash.

James Park, of Dunedin, New Zealand, has resigned the position of dean of the mining faculty which he has held for thirty years, during which time he has written several textbooks.

Noel H. Stearn, of St. Louis, Mo., is engaged as consulting geologist for the quicksilver deposits recently found in the Ouachita Mountains, Arkansas.

Louis A. Wright, of San Francisco and London, is on a trip to South and Central Africa.

Oliver Hall, previously with the Mond Nickel Company, and International Nickel Company, is now assistant manager of the Noranda Mines.

Ralph D. Parker is appointed general superintendent of mines for the International Nickel Company, succeeding Oliver Hall, and H. J. Mutz takes his place as superintendent of the Frood Mine.

The Governor of Oklahoma has turned over to the State University the records of the Oklahoma Geological Survey, and Dr. Charles E. Decker has been appointed to take charge of them.

Jyoji Suyehiro, director of the Earthquake Research Institute of the Tokyo Imperial University, addressed the Washington Academy of Sciences at their meeting of November 19, on the subject of Engineering Aspects of Earthquake Research in Japan.

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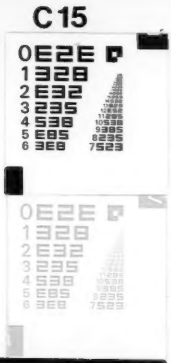
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